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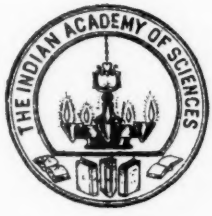

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COLOURS OF STRATIFIED MEDIA—I

ANCIENT DECOMPOSED GLASS

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1. Introduction

In a memoir published many years ago, Sir David Brewster (1863) described the structures found in ancient decomposed glass as well as the optical phenomena which they exhibit and illustrated them by reproductions of coloured drawings. The effects are most beautifully shown by specimens of antique glass-ware discovered in archæological excavations, but as these usually find their way into museums, few physicists have the opportunity of examining them and acquainting themselves with the facts by personal observation. At the Palais de la Découverte in the Paris Exposition of 1937, one of us saw in the section of Optics a very striking exhibit of an ancient vase of glass which had been excavated in Syria by the French archæologist M. Pupil. The remains of the vase together with numerous iridescent flakes resulting from its disintegration were placed in a plate-glass cabinet which was provided with viewing mirrors inclined at 45° to the vertical, and illuminated both from above and below, so that they could be seen simultaneously by transmitted and reflected light. The brilliance of the colours and the complementarity of the same as seen in transmission and by reflection were thus beautifully made evident. Through the kind offices of Prof. A. Cotton, a few flakes of glass from this exhibit were presented to us by M. Pupil. This gift enabled us to undertake the present investigation, which indeed we were desirous of doing, to supplement and complete our earlier work on the optical behaviour of decomposed glass of modern origin described recently in these *Proceedings* (1939). The important researches of M. Marcel Guillot (1934) on the production of iridescent laminæ on glass by chemical action should also be mentioned in this connection. His work indeed suggests the possibility that the processes which take place in glass very slowly under natural conditions may be reproduced in a more rapid and controllable manner by laboratory methods. Reference may also be made to the very interesting thesis by Dr. Coeling (1939) in which she has studied the absorption of water-vapour by films of decomposed glass and the resulting changes of colour.

The flakes derived from the Syrian vase reflect light strongly, exhibiting an almost metallic lustre, the colour of which varies greatly. The thicker flakes amongst those given to us exhibit a bluish-white silvery lustre, while the thinner ones exhibit other tints in which greens and oranges are the most striking colours observed at normal incidence. The flakes also exhibit vivid colours by transmitted light, being in this respect much superior to the specimens of decomposed glass of modern origin considered in our recent paper. The latter show scarcely any perceptible tints when observed in transmission, while on the other hand, the flakes from the Syrian vase show colours in transmitted light which in many cases are more striking than those seen by reflected light. The transmission colours for the thicker specimens tend towards a rich red, while the thinner flakes showed colours ranging over the whole spectrum from violet to red. It is thus evident that the development of colour occurs in antique glasses to a greater depth and in a more uniform manner than in the modern specimens. This makes it all the more desirable that they should be thoroughly studied.

Figs. 1 to 9 in Plates XXIII–XXIX accompanying this paper are photomicrographs of selected areas on the iridescent flakes of Syrian glass. Figs. 1, 2, 3, 4, 5 and 9 are pictures taken by monochromatic light in transmission with a petrographic microscope, a mercury arc lamp with a green ray filter being used as the source. Amongst these Figs. 2 and 9 were taken with the specimens placed between crossed nicols, while in taking the other photographs the polariser and analyser were removed. The fact that these photographs have been taken with monochromatic illumination has enabled us to notice and record certain characteristic features which would not otherwise have been evident. Figs. 6, 7 and 8 are pictures taken by reflection using the Leitz ultraopak microscope and white light. We have also obtained spectrograms (with incident white light) of the transmission and reflection by several of the flakes. These are reproduced as Figs. 10 (*a*) to (*f*) in Plate XXX. The present paper deals with the question of the structure of the decomposed glass and the origin of the colours which it exhibits as indicated by the microscopic examination and by the spectroscopic studies.

2. *The Lamellar Structure*

That decomposed glass is composed of thin laminæ adherent to each other is readily noticeable, even without the use of a microscope. The details of its structure however become more evident on microscopic examination and are quite remarkable and interesting. Fig. 1 (Plate XXIII) illustrates a common but by no means universal feature, namely that the laminæ, instead of being perfectly plane, consist of shallow cups shaped

like watch-glasses fitting together and dividing the surface of the flake into a large number of irregular polygons bounded by straight lines. The uniformity of curvature of the surface of the cups and the perfect sharpness of the lines in which they intersect are noticeable features. The former feature is shown in Fig. 1 by the perfectly concentric arrangement of the interference rings between the upper surface of the lamina and a plane sheet of mica which was laid over it when the photomicrograph was taken. It will be noticed that each of the polygons shows a ring system and that all of them are very much alike, in other words, that the curvatures of the cups are nearly the same, though their areas vary greatly. It will be noticed also that the dividing lines or sides of the polygons present a very similar appearance everywhere. These dividing lines are actually seen, however, as sets of diffraction bands running parallel to the boundaries : these have a bright centre when the microscope is focussed slightly above the plane of the lamina and a dark centre when the focus is below the plane. At critical focus the diffraction bands tend to become rather inconspicuous. From these observations it may be inferred that the dividing lines between the cup-shaped areas are extremely fine, indeed of razor-edge sharpness.

The hollow cup-like forms are naturally convex on one side of the lamina and concave on the other. This is noticeable on turning the lamina over on the stage of the microscope. The curvature of the surfaces may be made conspicuously evident by illuminating the lamina rather obliquely and observing it by reflected light. Fig. 6 shows this effect when the cavities are shallow and Fig. 8 when they are rather deep. The smoothness and uniformity of curvature of the cavities is indicated by the fact that they are capable of forming sharply defined images by reflection. This can be demonstrated with the reflecting microscope by pushing up or pushing down the objective as the case may be. Each cup-shaped area then shows an image of the illuminating annulus of the microscope, the surfaces themselves appearing dark except at the polygonal boundaries which continue to be seen faintly by reason of diffracted light (Fig. 7).

It is possible to find laminæ which do not exhibit the cup-like cavities referred to above, but have a smooth surface either wholly or except for discrete single or multiple cavities which they may exhibit. Examination of such a lamina under the polarising microscope between crossed nicols shows the surface as quite dark when there are no cavities, but as faintly illuminated when there are shallow cavities present. The deeper cavities appear strongly luminous round their inner margins and also exhibit the phenomenon of the black cross observed by Brewster (Fig. 9), which is due to the rotation of the plane of polarisation of the light in its passage through the oblique surfaces

of the lamina. Particularly beautiful are those cases in which there are numerous deep cavities which are discrete and do not meet to form polygonal figures. One such lamina as seen between crossed nicols is shown in Fig. 2 which exhibits quite a number of ellipsoidal cavities. Further, it will be seen that the luminosity is not confined to the edge of each cavity, but also extends within in the form of rings running parallel to its margin. In most cases, this appears to be a diffraction effect, but there is no doubt that occasionally also we may have multiple cavities forming concentric rings.

3. *Colour Effects*

The laminar structure of the decomposed glass is shown very prettily by the colours seen in transmission through the microscope. As was remarked by Brewster, areas of different colours will be noticed around the edges where the flakes have broken off unevenly. These correspond to the different thicknesses through which the light has to pass before reaching the eye. The boundaries of these areas act as diffracting edges and appear as sharp lines in the field of the microscope. Except when the laminæ have thus split off unevenly or when they have actually parted off from each other so as to admit a film of air between, the colours seen are very uniform over the surface of the flake, thereby showing that the glass, though laminar in structure, nevertheless consists of coherent layers in optical contact. Brewster's view that the colours are due to thin plates of air separating the laminæ thus appears to be incorrect. Indeed, the fact to which Brewster himself drew attention, namely that the elementary films of glass adhere with such force that it is difficult to separate them, is very strong evidence that they are in optical contact and not separated by continuous films of air.

The colour effects observed with those laminæ which exhibit cup-like depressions over their area are very pretty and significant. If the cups are very shallow, the colour of the laminæ is nearly uniform in tint over the area of the cup, though just at and near the boundary lines the colour is slightly different. When the cups are deep, the colour near their margins differs strikingly from that near the centre. This is due to the lamina being inclined to the line of vision round the periphery of a cup, whereas at its centre it is seen normally. To show that this is the correct explanation, we have merely to tilt the lamina on the stage of the microscope. The colours then change unsymmetrically, the part of the periphery of the cup which is now seen nearly normally has the colour which was originally observed at the centre, while the part at the periphery which is now still more inclined to the line of vision changes its colour still further in the sequence of increasing obliquity. It is equally

easy to follow the change of colour with increase of obliquity in these areas where there is no curvature, by merely tilting the lamina on the stage of the microscope. It is then seen that the sequence of colour is the same as over the areas which exhibit curvature. This demonstrates that the lamina is uniform in its structure and thickness in spite of the curvature and consequent apparent difference in colour over certain of its areas.

When optical contact between the layers of a lamina is actually broken, and a thin film of air enters, this makes itself evident by continuous variations of colour over the area of the flake as seen under the microscope. If the air film is sufficiently thick and, as must generally be the case, variable in thickness, regular bands of colour appear over such area. If more than one such film of air has found entry into a given flake, each film gives its own sequence of colour running along its direction of most rapid variation of thickness. We would then see two or more sequences of colour running across the film in different directions and intersecting each other. In view of the fact that the light transmitted by the flake as a whole is itself only a part of the spectrum, the colour sequences are quite different from the usual Newtonian scale. Even apart from this, they present peculiar features which become more intelligible when the incident light is monochromatic and the transmission through such film is examined under the microscope. Figs. 3, 4 and 5 reproduce three photomicrographs obtained in this way which will repay careful examination. It will be seen that each of them is traversed by a series of sharply defined bright lines running more or less parallel to each other in a relatively dark field and that in some cases, (particularly Fig. 3) two or more such series of lines running in different directions and intersecting each other are seen. That these effects are due to air films having entered the flake and broken optical contact between the laminæ is shown by gently pressing the flakes on the stage of the microscope. The bright bands are then seen to curve and move about in the field, but they recover their position when the pressure is removed. The fact that the band systems are more frequently seen near the edges of a flake where it is obviously easier for the laminæ to part company and admit a continuous film of air (see for instance the left-hand side of Fig. 3) is another indication that they do, in fact, arise in this way.

A remarkable feature noticed in Figs. 3, 4 and 5 is that in the interference bands which are so prominent, the maxima of illumination are sharp lines separated by broad dark bands. This feature suggests an analogy with the sharp interferences seen in a Fabry-Perot etalon and indeed is very similar to that seen under the microscope when a wedge-shaped film of air between the silvered faces of two plates of glass is examined by transmitted

monochromatic light. The two parts of the flake separated by an air-film behave therefore much as if they were heavily silvered surfaces in passing through which the light also undergoes multiple reflection, thereby sharpening the maxima. That this is the correct explanation of the sharpness of the maxima of illumination in these interference bands is indicated by the fact that the maxima are not so sharp when they are seen in air-films separated by very thin laminæ (see for instance, the bands towards the thin edge of the flake in Fig. 3). The laminæ chosen for obtaining Figs. 3, 4 and 5 were as nearly as possible uniform. They however exhibit a number of circular curved depressions which will be seen in the figures. When the interference bands due to the film of air are seen through such a depression, they appear wider apart or reduced in width, according as the curvature faces one way or the other. A fine example of a deep cavity is seen at the lower right-hand corner of Fig. 3, while several relatively shallow ones will be seen in Figs. 4 and 5. Three very curious examples of sharply-defined and concentric bright ring-systems will be noticed in Fig. 4; these however evidently arise in a different way, presumably as the result of the local separation of the laminæ by a film of air over these areas. The fact that a small dark and rather elongated nucleus can be seen at the centre of each of these ring-systems is probably a connected circumstance.

4. Effect of Immersion in Liquids

It has been remarked above that the laminæ in the flake are adherent to each other and form a continuous structure. The colours seen in reflection and in transmission must therefore be ascribed to this structure being stratified in such a manner that the refractive index of the medium varies quasi-periodically. An insight into the nature of the stratifications and of the resulting variations of refractive index is obtained by studying the effect of immersing the iridescent flakes in various liquids. Putting a small flake in the cavity on a microscope slide and allowing a little liquid to flow in, it will be noticed that the colours usually observed in transmission generally disappear or become inconspicuous, and that this is the case, whatever may be the refractive index of the liquid ranging from water ($\mu = 1{\cdot}33$) to methylene iodide ($\mu = 1{\cdot}74$). The colours of reflection however continue to be observable, but they are altered and enfeebled to an extent depending on the refractive index of the liquid used. To enable this effect to be studied critically, it is convenient to immerse the flake diagonally inside a small glass cell of square cross-section containing the chosen liquid which is then held facing the light. The reflection by the flake at an angle of 45° deviates the light incident on it by a right angle and may be viewed through the cell against a dark background. Even a feeble reflection may then be readily

recognised. Actually the iridescence is seen quite brightly if the flake is immersed in water ($\mu = 1{\cdot}33$), ether ($\mu = 1{\cdot}35$) or acetone ($\mu = 1{\cdot}36$) though a progressive diminution in intensity with increasing refractive index may be noticed. In hexane ($\mu = 1{\cdot}38$) and in paraldehyde ($\mu = 1{\cdot}40$) the iridescence is still conspicuous, though weaker. In chloroform ($\mu = 1{\cdot}44$) the coloured reflection is very weak but may still be seen. In carbon tetrachloride ($\mu = 1{\cdot}463$) it is practically unobservable. In benzene which has a higher refractive index ($\mu = 1{\cdot}50$) it is once again visible, while in chlorobenzene ($\mu = 1{\cdot}530$) and in bromobenzene ($\mu = 1{\cdot}56$) it is conspicuous. In carbon disulphide ($\mu = 1{\cdot}63$), it is quite bright, in fact, many times more intense than the reflection from the surface of a single plate of glass immersed in the liquid.

Placing the flake in a cell containing carbon tetrachloride, we may add a little chloroform and depress the index of the liquid, or add a little benzene, and raise its index until the reflection becomes observable. It is found in this way that an elevation of the refractive index to 1·470 or a depression to 1·460 is sufficient to make the reflection visible. The disappearance of the reflection may be explained by assuming that the decomposed glass has an open or "frame-work" structure into which the liquid, allowed sufficient time, can penetrate, and that when such liquid has a refractive index 1·465 the stratifications of optical density within the substance of the flake vanish and that it therefore ceases to reflect light. At the same time, according to this view, the refractive index of the saturated substance should itself be the same as that of the surrounding fluid, and its edges should therefore cease to be observable. This is actually found to be the case, and an application of the Becke immersion test under the microscope shows that the difference of refractive index between the flake and the surrounding fluid changes sign when the latter is altered from 1·460 to 1·470.

There is a definite change in the colour of the reflected light when the flake is immersed in the cell of liquid. This change is most readily seen in the colour of the normally reflected light, and is more conspicuous, the greater the refractive index of the immersion liquid. In general, it is found possible to compensate the change of colour produced by such immersion by viewing the flake obliquely. In other words, we can set off the effect of the increased index on the optical paths within the flake by the diminution in such paths due to a greater obliquity of incidence of the light on it. That an obliquity of the order of 45° or less is sufficient to achieve this indicates that the optical paths within the flake which are altered by the entry of liquid are not a very large part of the whole. It should be remarked also that though the effect of immersion is to diminish the intensity of the coloured

reflections and, as stated above, also to alter them appreciably, nevertheless the liveliness of the colours is actually improved instead of being impaired by such immersion. Further, the coloured reflections by the immersed films continue to be visible at greater obliquities instead of changing rapidly to white light as is the case when the flakes are observed in air. When the refractive index of the immersion liquid approaches that of the decomposed glass, the colours may be seen by reflection even at nearly grazing incidences.

The very low index (1·465) of the decomposed glass indicated by these observations is a noteworthy feature. It must be assumed that as the result of the decomposition and of the leaching out of some of the material in the course of long years, the average index, even of the more relatively compact parts of the glass has been reduced below that of normal glass. If the openings into which liquid can penetrate are taken into account, the effective reduction of the refractive index of the substance would of course be still greater.

5. *Spectroscopic Examination*

Each of the Figs. 10 (*a*), (*b*), (*c*), (*d*), (*e*) and (*f*) in Plate XXX relates to a distinct specimen of iridescent glass and contains a group of four spectra. The first and fourth of these are the spectra of the light source employed, namely, a filament lamp, and have been included for comparison with the second and third spectra in the same group which refer respectively to the light transmitted and reflected normally by the particular flake of glass.

It will be noticed that Figs. 10 (*a*) and 10 (*d*) present a remarkable contrast, indeed being almost exactly the opposites of each other. In the former, the entire spectrum is cut off in transmission except for a band at the red end which comes through, while in the latter, the whole spectrum is transmitted except a band at the red end which is cut off. *Per contra* again, in Fig. 10 (*a*) practically the whole spectrum appears in the reflected light except the red end which is greatly weakened, while in Fig. 10 (*d*), only the red end of the spectrum appears in the reflected light and the rest is cut off. Figs. 10 (*b*) and 10 (*e*) also present contrasting features of the same general description, though not of so marked a character. The principal feature in Fig. 10 (*c*) is the cut-off in the transmitted light of a portion of the spectrum in the yellow region and the appearance of the same region in the reflected light. Fig. 10 (*f*) shows no special feature except a large number of bands in the spectra of both the reflected and the transmitted light. The following table shows the colours of the normally transmitted and reflected light with the different specimens :

Table of Colours

Figure	Transmission colour	Reflection colour
10 (*a*) ..	Orange Red	Blue
10 (*b*) ..	Brick Red	Bluish White
10 (*c*) ..	Purple	Yellowish White
10 (*d*) ..	Blue-green	Red
10 (*e*) ..	Blue-green	Red
10 (*f*) ..	Neutral	Neutral

The vividness of the colours exhibited will be readily understood from the character of the observed spectra.

It is very remarkable that, as mentioned above, specimens of iridescent glass should exhibit two entirely different types of spectra, the first in which a limited region of the spectrum is strongly reflected while the rest of the spectrum is transmitted, and the second in which a limited region of the spectrum is transmitted while the rest is reflected. The first type of spectrum is characteristic of regularly stratified media with a large number of layers when the reflecting power of an individual layer is small. In such a case, the incident light is transmitted freely except in respect of the narrow band of wave-lengths for which the successive *reflections* reinforce each other by agreement in phase. This band of wave-lengths is selectively reflected and disappears from the transmitted light. If, however, the number of layers is small, the reflected spectrum contains a wider band of wave-lengths with subsidiary maxima on either side. There is little doubt that the transmission and reflection spectra illustrated in Fig. 10 (*d*) and (*e*) are to be explained in this general way, though it is clear that the regularity of the actual stratifications is far from being perfect. The spectra of the second type illustrated in Figs. 10 (*a*) and (*b*) resemble those observed when a beam of white light passes through a thin film of air between two heavily-silvered plates. In this case, as is well known, the effect of the large reflecting power of the surfaces is to reduce the transmitted light to a negligible intensity except in respect of those wave-lengths for which there is an agreement in phase of the successive *transmitted* pencils. Only the narrow bands of such wave-lengths appear in the spectrum of the transmitted light and the rest are cut off. The spectra

reproduced in Figs. 10 (*a*), (*b*) and (*c*) have evidently to be explained in this way. The difference in optical behaviour between the two classes of cases may be the result of either the spacings or their reflecting power or both being widely different. In this connection, reference may be made to a mathematical investigation by the late Lord Rayleigh (1917) in which he has shown that the passage of light through a regularly stratified medium may result in effects which are the opposites of each other, depending on the circumstances. In one set of cases, the effect of increasing the number of the stratifications is to make the reflection approach totality. In the second set of cases, the intensity of the reflected beam continues to fluctuate however large the number of stratifications might be, and might even vanish, in which case the light is completely transmitted. Rayleigh has discussed the criterion which distinguishes the two sets of cases and shown that the results are determined by the relation between the reflecting power of an individual stratification and the phase differences arising in passage through it.

The effect of tilting an iridescent lamina on the spectra of the transmitted and of the reflected light may be readily studied. In either case, the bands observed in the spectrum shift towards the violet and broaden with increasing obliquity. The actual effect of this on the observed colours is rather different in the two types of cases considered above. If, for instance, the transmission shows a dark band in the red region at normal incidence, the displacement of this towards the violet with increasing obliquity results in the colour seen changing from blue-green to blue, then to purple and yellow, while the reflected colours march from red to violet through all the rich tints of the spectrum. If, on the other hand, the transmission is initially limited to a band at the red end, the effect of increasing obliquity is to cause more and more of the spectrum from the red towards the violet to be freely transmitted. As the result of this, the transmission colour fades out rapidly, changing from red to a pale orange or yellow. The reflected colour which is initially a bluish white however becomes a richer and darker blue and finally tends towards indigo or violet.

As is to be expected, both the refleetion and the transmission are strongly polarised and in opposite ways at the Brewsterian angle of incidence. Here again, there are remarkable differences between the character of the effects observed in the two sets of cases. When the transmitted light includes the whole spectrum except a limited band of wave-lengths, striking changes are observed when the obliquely transmitted light is viewed through a polarising nicol. With the light vector in the plane of incidence, the film appears practically colourless, but with the light vector perpendicular to its

plane, it appears richly coloured. On the other hand, the films showing only a narrow transmission band at normal incidence are practically colourless at the polarising angle, the effect of rotating the observing nicol being merely to alter the intensity of the transmitted light. These same films however, show a remarkable increase in the richness of the colour of the *reflected* light at the polarising angle. The explanation of these facts will be clear in the light of the preceding discussion, when we remember that the reflecting power of an individual stratification is diminished for one of the components of the light vector and increased for the other by oblique incidence.

On immersing the iridescent flake in a cylindrical vessel of liquid of refractive index greater or less than that of glass, it is readily possible to observe the spectral character of the light reflected by it at various obliquities up to grazing incidence and to determine its state of polarisation. As remarked earlier in the paper, the transmission colours disappear on immersion in the liquid, but the reflected colours continue to be visible with great liveliness up to grazing incidence. They are also completely polarised at the Brewsterian angle of incidence on the liquid-glass boundary. These facts will be readily understood in the light of the preceding discussion, when it is recollected that the reflecting power of an individual stratification is greatly reduced when the lamina is immersed in a liquid. In the spectrum of the normally reflected light, narrow bands are observed which broaden out at oblique incidences, thus indicating that the iridescence is the co-operative effect of several laminations.

6. *Effect of Absorption of Liquid*

Very interesting phenomena are exhibited by an iridescent flake of glass when it is immersed in a liquid and then taken out and allowed to dry. As has already been mentioned, the flake appears nearly or quite colourless by transmitted light when wet, and it might be thought that the colour would reappear progressively as the drying proceeds. Actually, the colour reappears with remarkable suddenness and with extreme saturation. The phenomenon may readily be observed by holding up the film against the light from a window and watching it as it dries. Almost immediately the drying commences, the film turns black as viewed by transmitted light and silvery white as seen by reflected light. The film then gradually clears up, showing rich colours which fade away until finally the usual colours are restored. The phenomenon may be watched by transmitted light under the microscope, and this is specially advantageous when it is desired to scrutinise it in detail. A boundary of intense colour or opacity appears near the edge of

the colourless film and moves inwards as the drying progresses, finally covering the whole film. It then gradually weakens and disappears.

It is not necessary for observing these effects that the refractive index of the liquid should be different from that of glass. Indeed, carbon tetrachloride which, as we have seen, causes the reflection colours disappear, shows the effects described above just as effectively as any other liquid. If it is desired to prolong the duration of the stage of opacity, the flake may be kept under a microscope cover-slip, thus delaying the evaporation. Alternatively, a less volatile liquid may be used to wet the film. On the other hand, its drying may be speeded up by holding it in a current of hot air. This is a useful procedure when the liquid has been wetted by water or by a liquid of high boiling point.

These effects throw light on the structure of the iridescent films and show clearly that Brewster's explanation of the colours as due to thin films of air separating the layers of glass is untenable. The observations indicate that the glass has a continuous frame-work structure which is quasi-periodic or stratified. When the flake is completely wetted, the liquid penetrates into the minutest cavities and tends to render the glass optically homogeneous, though if its refractive index differs from that of glass, the stratifications persist and give observable colours by reflection. As the film dries, the liquid naturally withdraws first from the largest cavities but remains in the smaller pores and the minutest cavities. At the earliest stages of drying, therefore, the layers containing the minutest pores which continue to hold liquid have a higher refractive index and are optically more uniform than when the film is completely dry; on the other hand, the layers containing the larger cavities are empty of liquid and have the usual low refractive index. At this stage, therefore, the stratifications of refractive index are actually more pronounced than with the dry film and their reflecting power is accordingly greater. The reflection of light by the film therefore approaches totality.

The liquid held by a wetted film may be divided into at least three categories, (*a*) that held by the largest cavities, (*b*) that held by the finest pores, and (*c*) that molecularly adsorbed on the capillary surfaces. The rate at which the liquid evaporates and its temperature equilibrium with the vapour would naturally be different for the three categories. The colour of the film would depend on the nature and quantity of the liquid held and the manner in which it is distributed in the film. The detailed study of these effects for the iridescent films of ancient decomposed glass would obviously be of considerable interest and should enable the capillary structure of the glass to be investigated in detail. In this connection, it is important to

remember that the entry or withdrawal of liquid is far from being instantaneous. The flow of liquid through very minute capillaries is a slow phenomenon especially if it be viscous, and the capillary forces which cause the flow may sometimes vanish, *e.g.*, when the pore has a bottle-neck shape such as has been postulated to explain hysteresis phenomena in the adsorption of liquids. These considerations help us to understand the remarkable tenacity with which liquid is sometimes held by a flake of decomposed glass as is demonstrated by its influence on the observed colour.

7. *Effect of Mechanical Pressure*

That the decomposed glass has an open structure and that the colours arise from this structure being stratified or quasi-periodic is very clearly indicated by the observations already set out. It is a reasonable presumption that the structure is the result of the decomposition of the glass and the leaching out of the more soluble layers formed during its progress, the periodicity of the decomposition being probably analogous to the Leisegang effect as has been suggested by M. Guillot. On the assumption that the colours of the ancient glass are due to a periodic distribution of cavities or pores in its structure, we must expect that mechanical pressure should destroy or reduce the colours of the glass. The equipment may readily be tried by placing a small flake covered with a piece of cellophane on the stage of the microscope, and then pressing or rolling a blunt steel point firmly on its surface. The colour is then observed practically to disappear from the area of pressure and does not recover on its removal. The success of the experiment indicates that the colours in the Syrian vase do not arise from an alternation of solid layers of different refractive index in the material of the glass. The latter supposition would also be inconsistent with the observed easy penetration of liquid into the substance of the films.

8. *Summary*

The paper describes a detailed microscopic study of the structure of the films of decomposed glass derived from an ancient Syrian vase excavated by M. Pupil, and a spectroscopic examination of their iridescence. The investigation makes it clear that Brewster's explanation of the iridescence as due to films of air separating thin layers of glass is definitely erroneous. The material is optically and mechanically continuous, but has an open framework structure which is quasi-periodic or stratified. The stratifications are moderately regular with the result that in certain specimens, a limited region of the spectrum is totally reflected and the rest is freely transmitted, while in other specimens we have the opposite effect, namely that the whole of the incident light is reflected except for a limited region of the spectrum which

is transmitted. At oblique incidences and especially near the polarising angle, the colours seen vary with the azimuth of the vibration and in different ways in these two cases. Mechanical pressure destroys the structure and with it also the iridescence. Liquids can penetrate into the structure of the film, but the latter becomes optically homogeneous and ceases to reflect light only when the refractive index of the liquid is equal to that of the glass (1·465). When the wetted film commences to dry, the liquid withdraws first from the larger cavities while it is retained in the smaller pores. This results in the optical stratifications being actually more pronounced than in the dry film, with the consequence that the flake appears black by transmission and silvery white by reflection.

The paper is illustrated by reproductions of nine microphotographs and twelve spectrograms.

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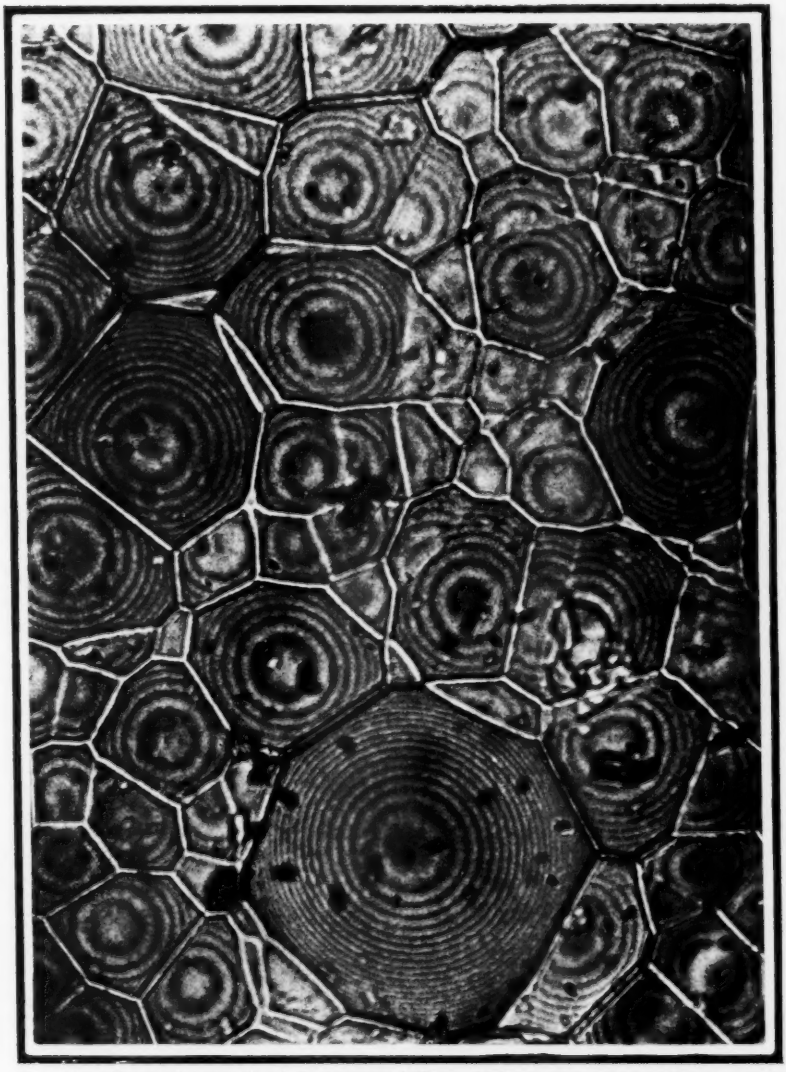

FIG. 1. Photomicrograph of Decomposed Glass in Monochromatic Light, showing Network of Curved Laminæ

FIG. 2. Photomicrograph of Decomposed Glass in Monochromatic Light under Crossed Nicols, showing Spherical and Ellipsoidal Cavities

FIG. 3. Photomicrograph of Decomposed Glass in Monochromatic Light, showing Laminar Edges, and Multiple Films of Air

FIG. 4. Photomicrograph of Decomposed Glass in Transmitted Monochromatic Light, showing Sharply Defined Fringes due to Intruding Air Films

FIG. 5. Photomicrograph of Decomposed Glass in Transmitted Light, showing Cavities and Fringes due to Intruding Air Films

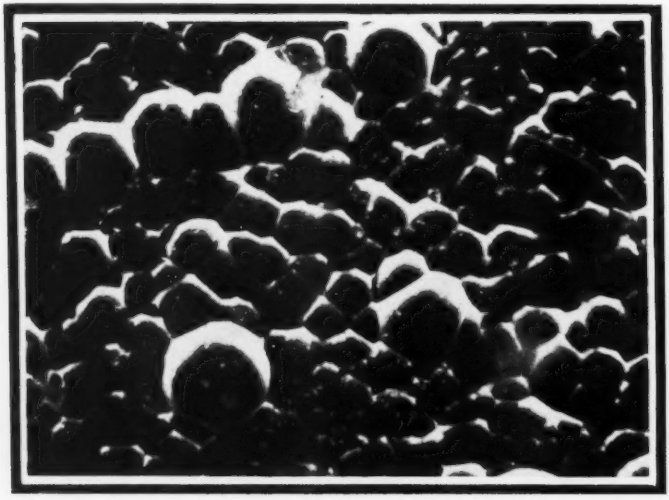

FIG. 6. Lamina with Hollows by Reflected Light

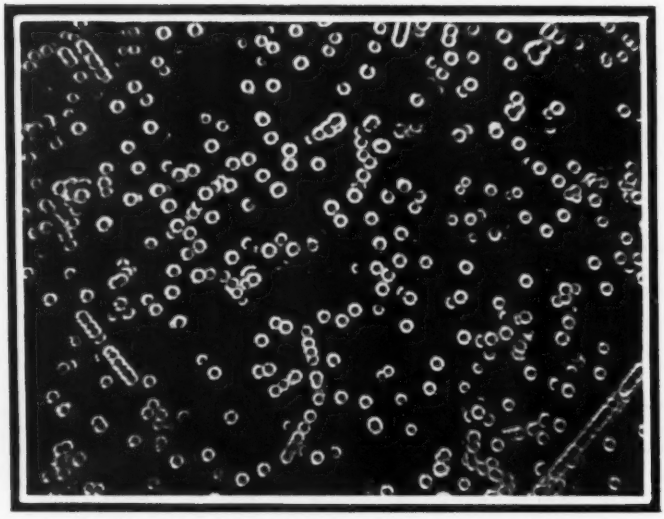

FIG. 7. Lamina with Hollows forming Optical Images of Light Source by Reflected Light

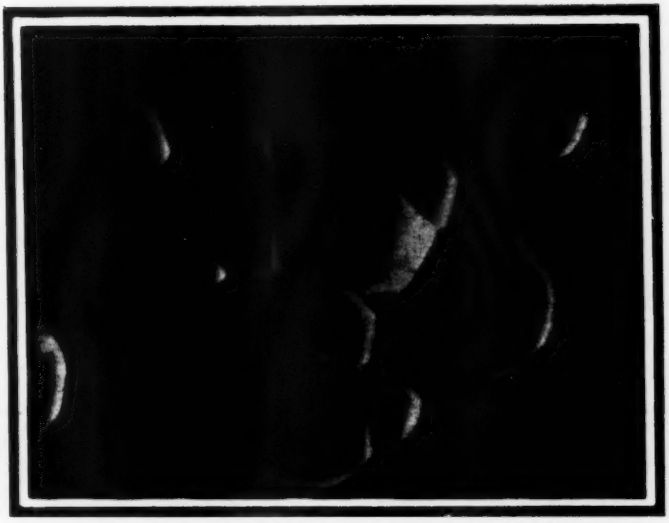

FIG. 8. Lamina with Hollows by Reflected Light

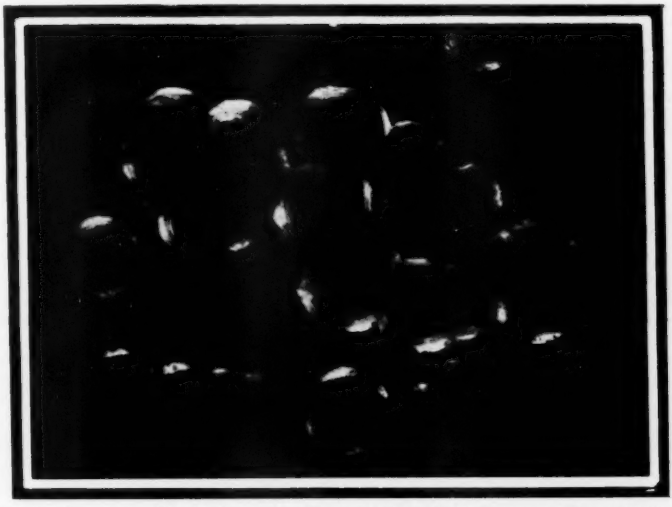

FIG. 9. Lamina with Hollows by Transmitted Light between Crossed Nicols

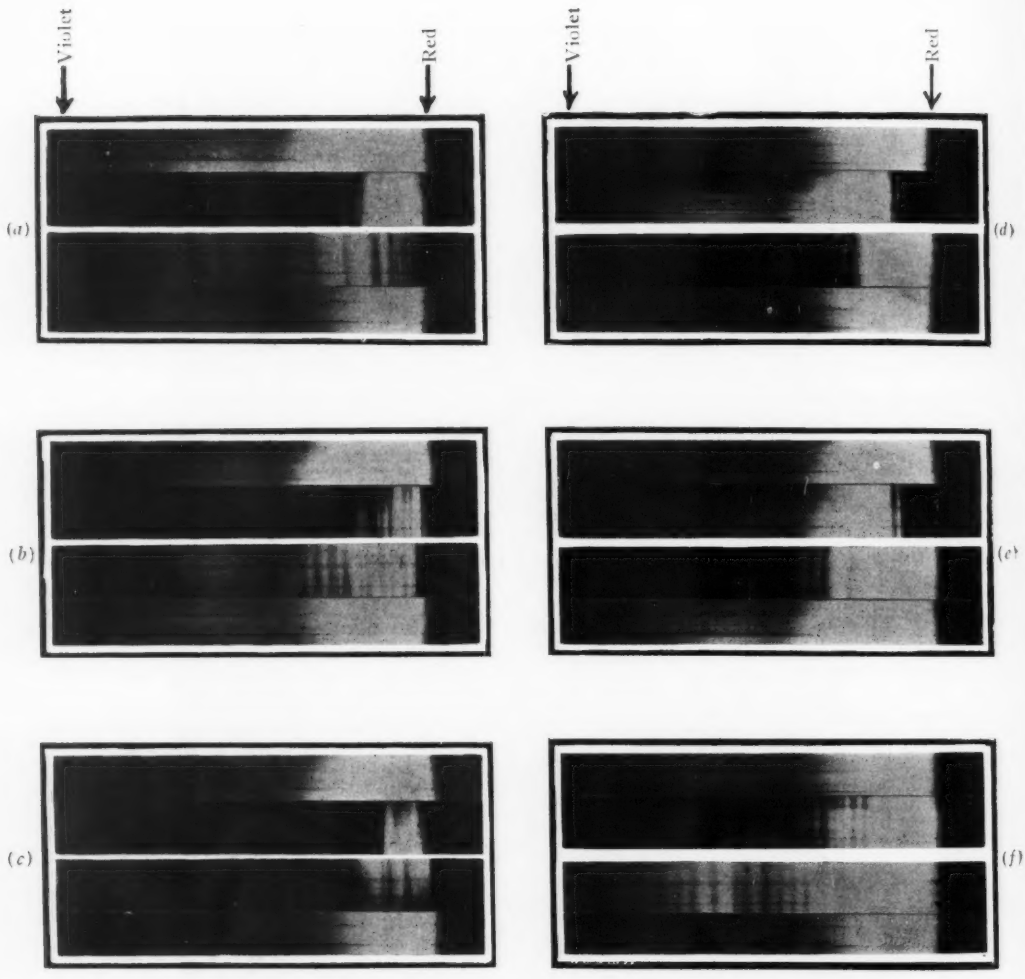

FIG. 10. (*a*), (*b*), (*c*), (*d*), (*e*) and (*f*). Spectrograms of Reflected and Transmitted Light of Decomposed Glass Films

COLOUR IN RELATION TO CHEMICAL CONSTITUTION OF THE PHTHALEIN DYES

Phthaleins of the Mixed Type

By Sikhibhushan Dutt

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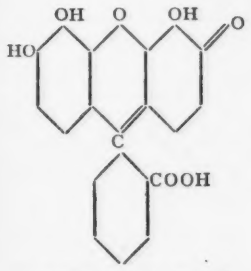
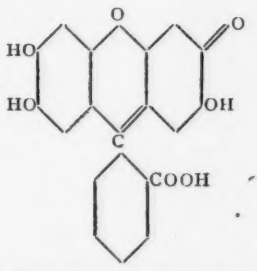
Received March 27, 1940

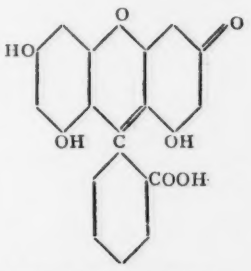
From the point of view of colour in relation to chemical constitution, perhaps some of the most interesting compounds in existence are the phthaleins obtained by the condensation of phthalic anhydride with aromatic phenols and amino-phenols, since they offer very great possibilities for generalisation. Dutt[1] has already pointed out in connection with the exposition of a "Theory of colour on the basis of molecular strain", that in the phthalein series, the nearer a hydroxy group is to the strained pyrone oxygen atom, the greater is the development of colour. Thus in alkaline solution, gallein is blue, hydroxyquinol-phthalein is pink and phloroglucinol-phthalein is orange, with absorption maxima at 5980 Å, 5540 Å and 4980 Å respectively :



Gallein (blue). 5980 Å

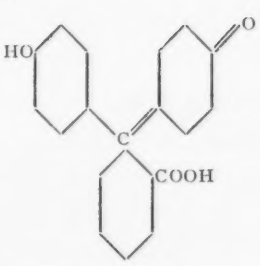


Hydroxyquinol-phthalein (pink) 5540 Å

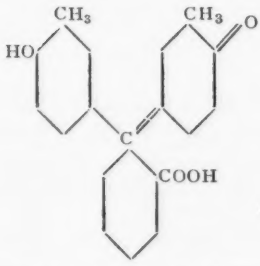


Phloroglucinol-phthalein (orange) 4980 Å

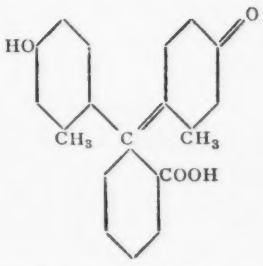
In the simpler phthaleins like phenol-phthalein and its higher homologues and analogues which do not contain any pyrone oxygen atom bridging the two benzene nuclei, the change of colour due to difference in the load is much less marked. For example, phenol-phthalein, *o*-cresol-phthalein and *m*-cresol-phthalein are all pink with slightly different shades and very close absorption maxima. Thus :



Phenol-phthalein (pink).
5550 Å



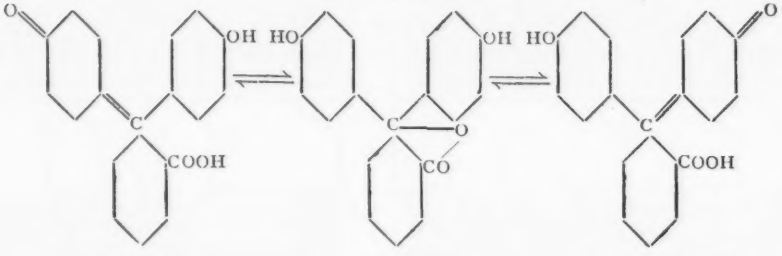
o-Cresol-phthalein (pink).
5565 Å



m-Cresol-phthalein (pink).
5555 Å

Phenol-phthalein is one of the simplest of organic compounds which passes from the colourless to the intensely coloured (pink or crimson) state by the action of alkali. This interesting and remarkable transition has been shown by the well-known and classical work of Otto Fischer, Hepp, Nietzki, Schroeter, Bernthsen and Friedlander, to be due to the conversion of the colourless lactonoid to the highly coloured quinonoid form :

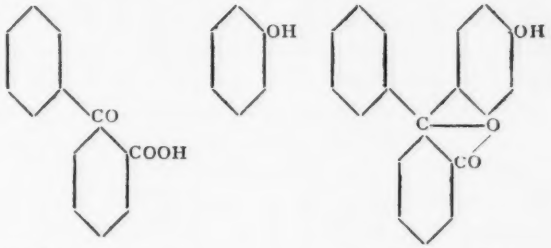
Phenol Phthalein.



Quinonoid Lactonoid Quinonoid

From the diagrams given above, it can be easily seen that lactonoid phenol-phthalein can tautomerise into two different and distinct quinonoid forms under the influence of alkali. Consequently it is not difficult to visualise, that under conditions in which all the three forms of phenol-phthalein are capable of existence, there will be twice as many highly strained and therefore deeply coloured quinonoid forms as comparatively unstrained and colourless lactonoid forms. It is for this reason that the alkaline solutions of phenol-phthalein are always deeply coloured, particularly in view of the fact that in alkaline solution not only the lactonoid form is difficult to exist due to extensive hydrolysis and opening up of the lactone ring, but the opportunity for the formation of the quinonoid form is also very great.

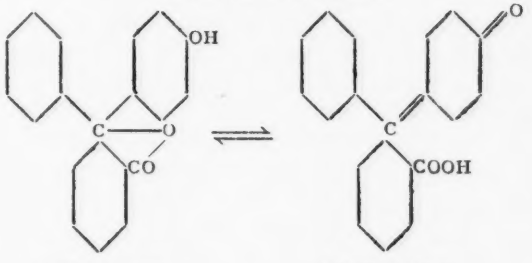
But if a condition could be created in which the tautomerism of the phenol-phthalein nucleus is rendered possible in only one of the two quinonoid forms mentioned above, the colour development of the substance is likely to be much less intense than in the case of phenol-phthalein. Such a condition exists in the case of hydroxy-diphenyl-phthalein obtained by the condensation of phenol with *o*-benzoyl-benzoic acid :



o-Benzoyl-benzoic acid. Phenol Hydroxy-diphenyl-phthalein

Under the influence of alkali, hydroxy-diphenyl-phthalein can tautomerise into only one possible quinonoid form :

Hydroxy-diphenyl-phthalein.



Lactonoid form Quinonoid form

Consequently from theoretical considerations it can be expected that hydroxy-diphenyl-phthalein will dissolve in alkali with less colour development than phenol-phthalein. From actual experimental evidence, this expectation has been realised and it has been found that hydroxy diphenyl-phthalein dissolves in alkali with only a pale yellow colour as contrasted with the intense pink colour of phenol-phthalein. In the solid state the substance is like phenol-phthalein, perfectly colourless.

Hydroxy-diphenyl-phthalein has been previously prepared in an impure state by Pechmann[2] by heating *o*-benzoyl-benzoic acid with phenol and

TABLE I

Mixed phthaleins derived from o-*benzoyl-benzoic acid* (*p* = *phthalein*)

Name of the compound	M. P. (° C.)	Appearance	Colour in solution of dilute NaOH	Absorption maxima in dilute alkaline sol. (Å)	Analyses. % Composition (Theoretical values in brackets)
Phenyl-phenol-p ..	92·5	Colourless glistening prismatic needles	Light yellow	4450	C =79·1 (79·4); H =4·9 (4·6)
Phenyl-*o*-cresol-p ..	133	,,	,,	4510	C =79·5 (79·7); H =5·3 (5·06)
Phenyl-*m*-cresol-p ..	146	,,	,, (hot)	4450	C =79·4 (79·7); H =5· 4 (5·06)
Phenyl-carvacrol-p ..	236	,,	Deep yellow (,,)	4480	C =80·2 (80·4); H =6·5 (6·1)
Phenyl-thymol-p ..	253	,,	,, (,,)	4480	C =80·4 (80·4); H =6·2 (6·1)
Phenyl-resorcinol-p ..	169	,,	Orange yellow	4710	C =75·2 (75·4); H =4·7 (4·4)
Phenyl-catechol-p ..	86	,,	red	5330	C =75·3 (75·4); H =4·5 (4·4)
Phenyl-quinol-p ..	241	,,	Deep yellow	4565	C =75·4 (75·4); H =4·6 (4·4)
Phenyl-α-naphthol-p ..	229	,,	,,	4900	C =81·5 (81·8); H =4·7 (4·5)
Phenyl-phloroglucinol-p ..	117	,,	,,	4650	C =72·0 (71·8); H =4·4 (4·1)
Phenyl-pyrogallol-p ..	126	,,	,,	4725	C =72·1 (71·8); H =4·2 (4·1)
Phenyl-*m*-dimethyl-amido-phenol-p (free base) ..	124	Pink glistening needles	Pink (alcohol)	5550	N =4·5 (4·4)
Ditto. (hydrochloride) ..	102	Pink glistening plates	,, (water)	5550	N =3·8 (3·8)

stannic chloride and he has described it as a colourless substance melting at 155° C., and dissolving in alkalies with a red colour like phenol-phthalein. This statement of Pechmann with regard to the behaviour of hydroxy-diphenyl-phthalein with alkali was rather surprising, since in accordance with the calculations of the present author from theoretical considerations, it ought to have a much weaker colour than phenol-phthalein. This led the present author to reinvestigate the problem, as the result of which it is now revealed that the *o*-benzoyl-benzoic acid used by Pechmann in 1881 for the preparation of hydroxy-diphenyl-phthalein melted at 87–94° C., which was apparently grossly contaminated with phthalic acid. Consequently the hydroxy-diphenyl-phthalein prepared by Pechmann from this material must have been largely admixed with phenol-phthalein, which accounted for the red colour given by his substance with alkali. The *o*-benzoyl-benzoic acid used in the present investigation was very carefully purified so as to make it perfectly free from phthalic acid, and the purest specimen on repeated crystallisation from xylene had a melting point of 129° C. On condensation with phenol in absence of any condensing agent or in presence of stannic chloride or a trace of concentrated sulphuric acid, hydroxy-diphenyl-phthalein is obtained which after exhaustive purification melted sharp at 92·5° C. and gave only a pale yellow coloration with dilute caustic soda. This was quite in accordance with expectations from theoretical considerations.

Encouraged by this promising result, the present author carried out further condensations of the pure *o*-benzoyl-benzoic acid with a number of phenols and amino-phenols and isolated the corresponding derivatives of diphenyl-phthalein in a state of great purity. The following substances were condensed with *o*-benzoyl-benzoic acid: phenol, *o*-cresol, *m*-cresol, carvacrol, thymol, catechol, resorcinol, quinol, pyrogallol, phloroglucinol, α-naphthol and *m*-dimethyl-amido-phenol. The absorption maxima of the condensation products have been determined and have been found to be considerably lower than those of the corresponding symmetrical phthaleins obtained from the respective phenol and phthalic anhydride (Table II).

In this connection it is interesting to note that similar reduction of the intensity of colour due to diminished tautomerism has been observed by Dutt and Agarwal[3] in the case of organic salts and metallic derivatives of isonitroso-1: 3-diphenyl-thiohydantoin as compared with the corresponding salts and derivatives of isonitroso-1 : 3-diphenylthio-barbituric acid prepared by Dharam Dass and Dutt.[4] Whereas the first compound can tautomerise into only one strained form, the second can do this in two strained forms as shown in the diagrams given below, and as a consequence, the salts and derivatives of the former are only crimson in colour (absorption maxima between

TABLE II

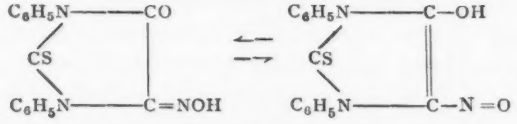
Comparison of the absorption maxima of the phthaleins derived from phthalic acid and o-benozyl-benzoic acid

(Figures indicate wave-lengths in Angstrom units)

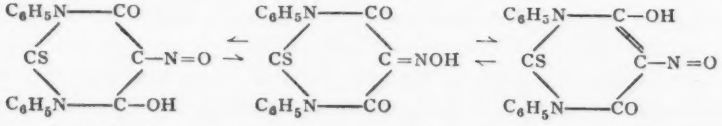
Compound derived from . . . and	Phthalic acid	*o*-Benzoyl-benzoic acid
Phenol	5550	4450
o-Cresol	5565	4510
m-Cresol	5555	4450
Carvacrol	5980	4480
Thymol	6030	4480
Resorcinol	4940	4710
Catechol	5960	5330
Quinol ..	5780	4565
α-Naphthol	5850	4900
Pyrogallol	5980	4725
Phloroglucinol	4980	4650
m-Dimethylamido-phenol ..	5550	5550

5320 Å and 5550 Å) but in the latter case they are green (absorption maxima between 5880 and 6610 Å), in spite of the fact that both the compounds possess almost identical molecular structures.

Isonitroso-1 : 3-diphenyl-thiohydantoin (crimson salts).



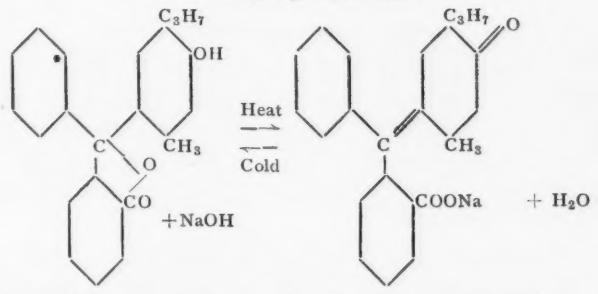
Isonitroso-1 : 3-diphenylthiobarbituric acid (green salts).



A further point of interest in connection with the phthaleins of the mixed type described in this paper is that the condensation products with

the higher homologues of phenol tend to become progressively insoluble in dilute caustic soda with increasing molecular weight. But on heating them with concentrated aqueous or alcoholic caustic soda, they all dissolve with a characteristic bright yellow coloration, undoubtedly due to the fission of the lactone ring and formation of a quinonoid structure. But this colour disappears on cooling due to the reformation of the insoluble lactonoid form which gets precipitated. Thus phenyl-thymol-phthalein behaves in the following manner on treatment with concentrated caustic soda :

Phenyl-thymol-phthalein.



Lactonoid (colourless and insoluble) Quinonoid (yellow and soluble)

This behaviour is also characteristic of phenyl-carvacrol-phthalein and phenyl-*m*-cresol-phthalein.

Experimental

Preparation of o-*benzoyl-benzoic acid.*—This acid was prepared by a slight modification of the original method described by Pechmann.[5] After six recrystallisations from boiling water and two from boiling xylene, the substance was obtained in glistening colourless prisms melting sharp at 129° C. The melting point did not rise any further after more crystallisations.

Condensation of o-*benzoyl-benzoic acid with aromatic phenols and amino-phenols.*—The condensations were effected by heating an equimolecular mixture (1/10 gram-molecule) of the acid and the phenol at 150–160° C. in an oil-bath. The condensations take place without the use of any condensing agent and usually take about 5–6 hours for completion, for the quantity of materials indicated. The end of the reaction is indicated by the molten mixture becoming completely solidified. The addition of two drops of concentrated sulphuric acid or about 1 c.c. of stannic chloride greatly facilitates the reaction which becomes completed within one-fourth of the time otherwise taken in absence of any condensing agent. The condensation products

are purified by repeated extraction with boiling water so as to remove any unchanged *o*-benzoyl-benzoic acid, and the insoluble products are then crystallised from dilute alcohol, ether or benzene. The phthaleins of the mixed type obtained in this way have remarkable power of crystallisation, but are generally always obtained in the form of glistening prismatic needles. In the solid state, they are all colourless with the exception of the compound derived from *m*-dimethylamido-phenol, which is pink. For the sake of abbreviation, the properties and absorption maxima of these compounds in dilute aqueous caustic soda have been given in tabular forms (Table I).

Summary and Conclusions

1. Mixed or unsymmetrical phthaleins obtained by the condensation of pure *o*-benzoyl-benzoic acid with aromatic phenols and amino-phenols, many of which have been prepared for the first time, have been shown to have much less intense colour development on solution in alkali than pure or symmetrical phthaleins obtained by the condensation of the same phenols and amino-phenols with phthalic anhydride.

2. The cause of the above interesting phenomenon has been traced to the existence of less intense tautomerism between the lactonoid and the quinonoid forms of the unsymmetrical phthaleins as compared with those of the symmetrical phthaleins. In some cases the tautomerism only begins to make itself manifested under drastic circumstances, that is in hot solutions of concentrated alkali.

3. The colour phenomena exhibited by the unsymmetrical and symmetrical phthaleins on treatment with alkali are quite comparable with similar phenomena exhibited by isonitroso-1 : 3-diphenyl-thiohydantoin and isonitroso-1 : 3-diphenylthiobarbituric acid under identical conditions as studied by Dutt and his pupils, and due to the same cause.

The author wishes to express his best thanks to Messrs. J. N. Tayal and B. M. S. Agarwal for carrying out some of the analyses.

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2. H. Pechmann, *Ber.*, 1881, **13**, 1608.
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4. I. N. Dharam Dass and S. Dutt, *Ibid.*, 1938, **8**, 145.
5. H. Pechmann, *Ber.*, 1881, **13**, 1612.

STUDIES IN TURBINE GEOMETRY—IV THE TOPOLOGY OF ORIENTED AND NON-ORIENTED LINE ELEMENTS IN THE INVERSIVE PLANE

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Received April 25, 1940

The inversive plane may be defined as the totality of all real points on the circumference of a circle and in its interior together with the inverses of the latter and an ideal "point at infinity" which is adjoined to correspond to the centre of the circle. Such a point set is carried over in a biuniform bicontinuous manner into itself by every operation of the inversive group, that is by inversion in a circle or by a succession of inversions.

The inversive plane ω differs from the Euclidean plane in being a closed point set, and from the projective plane in closure being effected by an ideal point and not by the adjunction of an ideal line. The totality of points in the interior of a circle gives a topological image of the Euclidean plane, while if the circumference be also included and diametrically opposite points considered identical, we have a set homeomorphic with the projective plane. To get a topological image of the inversive plane we shall have to consider all points on the circumference as identical.

By continuous deformation and coincidence of points considered identical, this may be transformed into the points on the surface of a sphere in 3-space, *i.e.*, a 2-sphere Ω. A homeomorphism may be established between the 2-sphere Ω and the inversive plane ω by stereographic projection, the centre of projection corresponding to the "point at infinity".

As an arithmetical continuum the points of the Euclidean and projective planes may be defined as

(1) real number pairs x, y subject to $x^2 + y^2 < a^2$ (Euclidean plane).

(2) ratios $x : y : z$ of real number triads not all 0 (projective plane).

The inversive plane may be specified in a similar manner by

(3) the ratios $x^2 + y^2 : xz : yz : z^2$ where x, y, z are real numbers not all zero.

By making the points defined by $x : y : z$ in (2) and (3) correspond, we have a correspondence between the projective and inversive planes which is (1–1) except for points on the line $z = 0$ of the former all of which correspond to (1, 0, 0, 0) of the latter.

2. Stereographic projection provides more than a mere mode of establishing a correspondence between ω and Ω. The transformations of the inversive group are carried over into projective transformations carrying Ω into itself and hence the inverse group into the automorphic collineation group of Ω in the projective space S_3. This is a mixed 6 parameter group G'_6 consisting of two continuous systems of transformations G_6, H_6. One system G_6 corresponds to an even number of inversions and carries each oriented circle into another circle oriented the same way, while the transformations of H_6 correspond to an odd number of inversions and reverse the orientation. They correspond respectively to the homeographies and antigraphies of the inversive plane, each general homeography being expressible as the product of 4 inversions and each antigraphy as the product of 3 inversions.[1] The homeographic transformations G_6 constitute a sub-group of G'_6.

3. *Oriented Line Elements of the Inversive Plane*

The totality of line elements of the inversive plane constitute a 3-dimensional aggregate whose topological character differs according as they are considered oriented one way or oriented both ways, *i.e.* (non-oriented).[2] In either case each line element of the inversive plane corresponds by stereographic projection to a line element and hence to a tangent line to the sphere Ω.

Locally, the line elements in a small region constitute a product manifold—that of a circle and a 2-cell. The outstanding characteristic of the totality of all line elements in the large is that *it is not a topological product*. This statement is equivalent to the result that it is not possible to associate with each point of the sphere a line element, oriented or otherwise, so that they vary in a continuous manner.[3] Were such a covering of the sphere

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[1] *Vide* Morley : *Inversive Geometry*, p. 64.

For a discussion of the invariant theory of the inversion group by quaternary and double binary methods reference may be made to an important paper on the subject by E. Kasner : *Transactions of the American Mathematical Society*, Vol. I, pp. 430–98.

[2] " Studies in Turbine Geometry—I," *Jour. Ind. Math. Soc.*, pp. 97, (1.1).

[3] This result is due to Poincare. Bronwer extended it to all n-spheres for which n is even and showed that it fails when n is odd. Thus on the 3-sphere $x_0^2+x_1^2+x_2^2+x_3^2 = 1$ a continuous vector distribution is given by means of the components (x_1, x_0, x_3, x_2) where x is a point on the sphere. Alexandroff : " Topologie I," p. 481.

with line elements possible, we should be able by continuous rotation of all the elements to represent all line elements on the sphere as the topological product of the 2-sphere and a circle. In fact in the case of no two dimensional variety except the anchor ring, which is itself a topological product, do the totality of line elements constitute a topological product.[4]

If the line elements be oriented, we may fix one of them l as reference initial element. Every other element m may be obtained from l by a unique rotation of the sphere about a suitably chosen diameter through an angle θ not exceeding two right angles. This rotation may be represented by a vector of length θ drawn from the centre O along that diameter one way or the other according to the sense of the rotation. We associate with the line element l itself the centre O of the sphere. We thus have a representation of all oriented line elements of the sphere by points in the interior and on a sphere of radius π. Diametrically opposite points of this sphere must be considered identical since a rotation about a diameter through $+\pi$ or $-\pi$ carries l into the same element. Hence the totality of all oriented line elements of Ω is homeomorphic with a projective manifold of 3-dimensions. An actual representation of the totality of oriented line elements of the inversive plane on a projective 3-space, or what is its equivalent, a representation of the rotations of a sphere about its centre by means of 4-homogeneous parameters may be obtained by means of the quaternion formula :

$$x' = a^{-1} xa$$

where x, x' are vectorial quaternions representing the old and new positions of the point and $a = a_0 e_0 + a_1 e_1 + a_2 e_2 + a_3 e_3$ the quaternion which determines the rotation. All the a's are real numbers and it will be seen that the transformation $x \to x'$ is determined by the ratios $a_0 : a_1 : a_2 : a_3$, *vide* E. A. Weiss : *Einfuhrung in die Liniengeometrie und Kinematik*, p. 96.

There are two types of fundamental closed curves in projective space—the straight line and the circle. In the first case closure is dependent on the identification of diametrically opposite points on the bounding sphere, while in the second it is independent of such identification. The former corresponds to a continuous succession of line elements in which the total rotation of the element about its middle point is 2π such as a star or a turbine. The latter corresponds to a succession of elements in which the total rotation is zero.

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[4] *Vide* W. Threlfall: "Raume aus Linienelemente," *Jahresbericht der Deutschen Mathematiker Vereinigung*, 1933, **42**, p. 108.

4. *Non-Oriented Line Elements in the Inversive Plane*

The totality of non-oriented line elements of the inversive plane or of the 2-sphere are represented twice over on the oriented line elements of Ω. These latter correspond, as we have seen, to points on a projective 3-space which again is covered twice over by points on a 3-sphere. Since the fundamental group of a 3-sphere is the identity, we may take it to be the universal covering manifold (Universelle Überlagerungsmannigfaltigkeit). The fundamental group of M is thus of order 4. From the finiteness of the fundamental group it follows that the closed manifold M is orientable.[5]

Each non-oriented line element of the sphere Ω in a projective 3-space S_3 determines a tangent line to the sphere. By means of Plücker's line co-ordinates p_{ij} we represent all lines in S_3 by points in a quadric Q of signiture zero in a projective S_5 and, in particular, the tangent lines of Ω by the section of Q with another quadric Q′ corresponding to a special quadratic complex. The intersection variety V_3^4 in S_5 is a topological image of the manifold M.

5. *Fibred Spaces*

Both the non-oriented and oriented line elements of a 2-sphere constitute varieties known as fibred spaces, the fibres corresponding to the line elements with the same point (stars). For we have here closed 3-dimensional varieties whose points group themselves into closed curves—the fibres. Through each point passes a unique fibre and each fibre possesses a neighbourhood of fibres, *i.e.*, a subset of fibres which may be represented as the topological product of a 2-cell and a circle. The variety of decomposition or base variety of the fibration, *i.e.*, the variety obtained by taking each fibre as an element is the 2-sphere Ω itself.[6]

The problem of determining all the fibred spaces of n-dimension whose variety of decomposition of dimension d is known does not appear to have been solved in general. However, when $n = 3$ and $d = 2$ which is our special case the problem can be resolved completely. We have an infinity of fibred spaces with a 2-sphere for the variety of decomposition each of which is completely characterised by an integer $b > 0$. For $b = 0$ it is the topological product of the 2-sphere and the circle. For $b > 0$ we have[7] a

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[5] Threlfall : "Aufgabe 135," *Jahresbericht d. Deutschen Matth. Vereinigung.*

[6] For discussion of fibred spaces in which the fibres are of dimensions higher than unity reference may be made to H. Whitney, "Sphere Spaces," *Proc. of the National Academy of Sciences of the U.S.A.*, Vol. 21, No. 7.

[7] Threlfall : "La Topologie der varieties," *L Enseignement Mathematique*, 1936, p. 251.

lenticular space whose coefficient of torsion is b, and whose fundamental group is cyclic and of order b.

Such a lenticular space[8] is bounded by two equal spherical caps intersecting in a circular edge C. The circumference of C is divided into p equal segments. Each point on either of the bounding caps is identified with the point of the other obtained by a reflection in the plane of C and a rotation about the axis of C through an angle $2\pi q/p$ where $0 \leqslant q \leqslant p/2$ is an integer prime to p. The p vertices, edges and faces are all identical for the resulting polyhedron so that its Euler characteristic is 0. For $p = 1$ and $p = 2$ we obtain respectively a 3-sphere and a projective 3-space. The lenticular space obtained when $p = 4$, $q = 1$ may be identified with the totality of all non-oriented line elements of the inversive plane. Its torsion coefficient is 4. Its Betti numbers p^i are connected by the relation

$$-p^0 + p^1 - p^2 + p^3 = \text{Euler-Poincare Characteristic} = 0,$$

$p^0 = 1$ for a connected manifold, while $p^3 = 1$ since the manifold is orientable. Hence $p^1 = p^2$ both being zero in this case.

6. The actual representation of the non-oriented line elements of Ω on such a lenticular space may be effected as follows : We take a fixed oriented reference line element and associate with every other line element of Ω a quaternion

$$x = x_0 e_0 + x_1 e_1 + x_2 e_2 + x_3 e_3$$

as in para 3 but of unit norm., so that

$$\Sigma : \; x_0^2 + x_1^2 + x_2^2 + x_3^2 = 1$$

diametrically opposite points of Σ being considered identical. The reference element corresponds to $\pm e_0$. A rotation through π (*i.e.*, a reflection in the axis of rotation) is represented by a quaternion whose scalar component x_0 vanishes. The rotation which reverses the direction of the reference element is of this type and may be taken to be $\pm e_1$. The product $e_1 x$ corresponds to a reversal of the orientation of the line element and then a rotation x. Hence it corresponds to the same element as x but with its orientation reversed. Since our line elements are not oriented we identifiy x and $e_1 x$. Since e_1 is cyclic and of order 4 we have tetrads of identical elements x, $e_1 x$, $-x$, $-e_1 x$.

Now $$e_1 x = -x_1 e_0 + x_0 e_1 - x_3 e_2 + x_2 e_3$$

so that the transformation $x \to e_1 x$ is equivalent to a simultaneous rotation of the $x_0 x_1$ plane and of the $x_2 x_3$ plane about the origin through one right

[8] Siefert-Threlfall : *Lehrbuch. der Topologie*, p. 210.

angle. We project Σ stereographically on the 3-space $x_1 = 0$ from the vertex (1, 0, 0, 0). The projection of the circle on the $x_0 x_1$ plane is the x_1 axis which we now endow with an elliptic metric in which the separation of two points is measured by the angle between the two corresponding points on the $x_0 x_1$ circle. A simultaneous rotation in the $x_0 x_1$ and $x_2 x_3$ planes is now projected into a kind of helicoidal motion in the 3-space. The lenticular region is one whose base surface is carried over into the other by this movement.[9]

[9] Trelfall : *loc. cit.*, p. 245–7.

A GEOMETRICAL PROOF OF A THEOREM ON SPINORS

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The theory of spinors is an off-shoot from Dirac's relativistic theory of the electron. If a pair of complex quantities (ψ_1, ψ_2) transform into another pair (ψ_1', ψ_2') so that

$$\begin{aligned} \psi_1' &= a_{11}\psi_1 + a_{12}\psi_2 \\ \psi_2' &= a_{21}\psi_1 + a_{22}\psi_2 \end{aligned} \quad \text{where} \quad \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = 1 \qquad (1\cdot1)$$

(ψ_1, ψ_2) are said to be the components of a spinor. A set of quantities $A_{r,k-r}$ where k is fixed and r varies from o to k, and which transform like $\psi_1^r \psi_2^{k-r}$ form a spinor of rank k. The complex-conjugate pair $(\bar{\psi}_1, \bar{\psi}_2)$ generates the complex-conjugate spinors. Van der Waerden and Uhlenbleck have shown that *to every skew symmetric self-dual tensor of rank* 2 *corresponds a symmetric spinor of rank* 2.[1] *Whittaker has shown that if the above tensor is a null tensor, it corresponds to a spinor of rank* 1.[2] The object of this note is to give a geometric proof of the above results.

2. Let us first take up the geometric representation of spinors and tensors. In space-time, with the metric of special relativity

$$ds^2 = dx^{1^2} + dx^{2^2} + dx^{3^2} - dx^{4^2} \qquad (2\cdot1)$$

$x^4 = ct$, the contra-variant vectors at any point form a centred affine tangent space, the null vectors forming the null cone

$$x^{1^2} + x^{2^2} + x^{3^2} - x^{4^2} = 0. \qquad (2\cdot2)$$

The section of the cone, by the hyper-plane at infinity in that space is a quadric Q. Let the generators of one system λ of Q be denoted by the parameter $\psi_1 : \psi_2$ and those of the other system μ by $\phi_1 : \phi_2$. Every real positive transformation keeping (2·2) invariant *i.e.* every positive Lorentz

[1] Van der Waerden : *Gottinger Nachrichten*, 1929, p. 100; Uhlenbleck and Laporte, *Physical Review*, Vol. 39, pp. 1380–87. In the above articles, we have a good introduction to the theory of spinors.

[2] E. T. Whittaker : "On the relations of the tensor calculus to spinor calculus," *Proc. Royal Soc.*, 1937, Vol. 158.

transformation, keeps Q invariant and carries each system of generators into itself. Further if the generator $\psi_1 : \psi_2$ is transformed into the generator $\psi_1' : \psi_2'$, it is known that

$$\begin{aligned} \psi_1' &= a_{11}\psi_1 + a_{12}\psi_2 \\ \psi_2' &= a_{21}\psi_1 + a_{22}\psi_2 \end{aligned} \quad \text{where} \quad \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} = 1$$

Hence (ψ_1, ψ_2) form a spinor. Conversely any spinor (ψ_1, ψ_2) can be represented by the generator of the λ-system with the parameter $\psi_1 : \psi_2$. Then $(\bar{\psi}_1, \bar{\psi}_2)$ can be represented by the generator of the μ system passing through the real point on the first generator.[3]

Let x^1, x^2, x^3, x^4 be the co-ordinates of any real point on Q. The quantities $x^4 - x^3$, $x^1 - ix^2$, $x^1 + ix^2$, $x^4 + x^3$ transform like a mixed (1, 1) spinor.[4] If x, y be any two points, the co-ordinates $p^{rs} = x^r y^s - x^s y^r$, $r, s = 1, 2, 3, 4$; $r \neq s$, of the line joining the two points transform like the components of a skew-symmetric tensor. Any general covariant skew-symmetric tensor a_{rs} can be represented by the linear complex $a_{rs} p^{rs} = 0$.

If the skew-symmetric tensor is self-dual with respect to the ground form (2·1), then

$$a_{12} = \pm i a_{34}, \; a_{23} = \pm i a_{14}, \; a_{31} = \pm i a_{24}$$[5]

(the positive or the negative sign is to be taken throughout). In this case the corresponding linear complex L is self-dual with respect to Q. The geometric interpretation is that the polarity defined by Q carries L into itself, and the null-system defined by L carries Q into itself.[6] If the tensor is a null tensor, the invariant $a_{12}a_{34} + a_{23}a_{14} + a_{31}a_{24} = 0$, and the linear complex L is special *i.e.* it consists of all lines intersecting a fixed line.

3. The proofs of the results of Van der Waerden, and Whittaker depend upon the following geometric theorem.

If a linear complex L is self-dual with respect to a quadric Q, the null-system defined by L carries every generator of one system of Q into itself and determines an involution on the generators of the other system. (3·1)

As observed already, the null-system of L carries Q into itself. Further it must keep invariant each system of generators of Q. For otherwise, it must interchange the two systems. In this case, the polar line l' of every generator l of one system, say the λ-system, being a generator of the second

[3] For the above geometric representation of spinors, see Veblen Rice Institute Pamphlet, 1934.

[4] The indices of x and y are not powers to which they are raised, but they indicate the contravariant nature.

[5] See Uhlenbleck, *loc. cit.*

[6] See § 4, where it is shown analytically.

system must intersect l, which is impossible. Hence l and l' belong to the λ-system. In general l and l' are distinct. The relation between l and l' is involutory, and we thus have an involution on the λ-system. Since every generator of the μ-system intersects a pair of polar lines l and l', it must belong to L.

Suppose l' coincides with l for every l, *i.e.*, L carries every generator of the λ-system into itself. Then it must determine an involution on the μ-system. Otherwise it must carry the μ-system also into itself, which is impossible, since to a linear complex cannot belong, both the systems of generators.[7]

In either case, every generator of one system is invariant, and an involution is determined on the other system. Thus we have (3·1).

To get the result of Van der Waerden, let us take the self-dual linear complex L determined by the given skew-symmetric self-dual tensor. Suppose it determines an involution on the λ-system. Any involution can be expressed analytically in the form

$$A\lambda\lambda' + B(\lambda + \lambda') + C = 0$$

Since $\lambda = \dfrac{\psi_1}{\psi_2}$ we have

$$A\psi_1\psi_1' + B(\psi_1\psi_2' + \psi_1'\psi_2) + C\psi_2\psi_2' = 0.$$

Hence the coefficients A, B, C are the components of a contra-gradient symmetric spinor of rank 2. If the involution is determined on the μ-system, we get a complex conjugate spinor.

Suppose the tensor is a null tensor. Then L is special, consisting of all lines intersecting a given line l. Since L is self-dual with respect to Q, l must be carried over into itself by the polarity with respect to Q. Hence l must be a generator of Q, say of the λ-system. Then the null-system of L carries every generator of the λ-system into l. Every generator of the other system must belong to L, since intersects l. The involution determined on the λ-system is degenerate, the double lines coinciding with l. Since the parameter $\psi_1 : \psi_2$ of l transform like a spinor, we have Whittaker's result.

4. We shall now obtain the results analytically and get the actual components of the spinor, when those of the tensor are given.

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[7] This is proved in § 4. It is also seen as follows :—

Suppose L contains both the systems. The null system defined by L will carry the tangent planes of Q through any point P not on Q, into the points of contact. Hence, the null plane of P is the plane of contact of tangent planes from P, which it cannot be, since it does not pass through P.

The two systems of generators of the quadric $x^{1^2} + x^{2^2} + x^{3^2} - x^{4^2} = 0$ are given by

$$\frac{x^1 + ix^2}{x^4 - x^3} = \frac{x^3 + x^4}{x^1 - ix^2} = \lambda = \frac{\psi_1}{\psi_2}$$

$$\frac{x^1 - ix^2}{x^4 - x^3} = \frac{x^3 + x^4}{x^1 + ix^2} = \mu = \frac{\overline{\psi}_1}{\psi_2}$$

The co-ordinates of the generator λ are

$$p^{34} = u_{12} = -2\lambda i$$
$$p^{14} = u_{23} = -i(1 - \lambda^2)$$
$$p^{24} = u_{31} = \lambda^2 + 1$$
$$p^{31} = u_{24} = -i(1 + \lambda^2)$$
$$p^{12} = u_{34} = -2\lambda$$
$$p^{23} = u_{14} = \lambda^2 - 1$$

The line co-ordinates of the μ generator are :

$$p^{34} = u_{12} = 2\mu i$$
$$p^{14} = u_{23} = i(1 - \mu^2)$$
$$p^{24} = u_{31} = \mu^2 + 1$$
$$p^{23} = u_{14} = \mu^2 - 1$$
$$p^{31} = u_{24} = i(1 + \mu^2)$$
$$p^{12} = u_{34} = -2\mu$$

Hence the λ generators belong to the net of linear complexes.

(A) $p^{12} + ip^{34} = 0 \qquad p^{23} + ip^{14} = 0 \qquad p^{31} + ip^{24} = 0$

The μ generators belong to the net

(B) $p^{12} - ip^{34} = 0 \qquad p^{23} - ip^{14} = 0 \qquad p^{31} - ip^{24} = 0$

Any linear complex is self-dual with respect to Q if

$$a_{12} = \pm ia_{34}, \qquad a_{23} = \pm ia_{14} \qquad a_{31} = \pm ia_{24}.$$

Hence the two systems of self-dual complexes are

(C) $k_1(p^{23} + ip^{14}) + k_2(p^{31} + ip^{24}) + k_3(p^{12} + ip^{34}) = 0$

(D) $k_1(p^{23} - ip^{14}) + k_2(p^{31} - ip^{24}) + k_3(p^{12} - ip^{24}) = 0.$

Obviously C contains all lines of the λ system and D those of the μ system. Also since C is apolar to all the complexes B, it carries the μ system also into itself. But it cannot carry every generator of the μ system also into itself; for in this case C must be a linear combination of the complexes B

which is impossible. Hence it determines an involution on the μ system. The double lines are those which belong to C. Hence

$$2k_1(\mu^2 - 1) + 2k_2 i(1 + \mu^2) - 4k_3\mu = 0 \qquad (4\cdot1)$$

Hence the involution determined by them is

$$\mu\mu'(k_1 + k_2 i) - k_3(\mu + \mu') + (k_2 i - k_1) = 0$$

Substituting for μ, $\frac{\bar{\psi}_1}{\bar{\psi}_2}$ we have,

$$\bar{\psi}_1\bar{\psi}_1'(k_1 + k_2 i) - (\bar{\psi}_1\bar{\psi}_2' + \bar{\psi}_2\bar{\psi}_1')k_3 + (k_2 i - k_1)\psi_2\bar{\psi}_2 = 0 \qquad (4\cdot2).$$

We thus have:—

To a skew symmetric self-dual tensor a_{rs} corresponds the symmetric spinor $\alpha^{\dot{k}\dot{l}}$ where

$$\left.\begin{aligned} a_{23} &= -ia_{14} = k_1 \\ a_{31} &= -ia_{24} = k_2 \\ a_{12} &= -ia_{34} = k_3 \end{aligned}\right\} \quad (4\cdot3) \qquad \text{and} \qquad \left.\begin{aligned} \alpha^{\dot{1}\dot{1}} &= k_1 + k_2 i \\ \alpha^{\dot{2}\dot{2}} &= k_2 i - k_1 \\ \alpha^{\dot{1}\dot{2}} &= \alpha^{\dot{2}\dot{1}} = -k_3 \end{aligned}\right\} (4\cdot4)$$

If the skew-symmetric self-dual tensor is a null tensor, so that $k_1^2 + k_2^2 + k_3^2$, vanishes (4·1) is a perfect square and the double lines of the involution coincide with the μ generator whose parameter is given by

$$\frac{\bar{\psi}_1}{\bar{\psi}_2} = \sqrt{\frac{k_2 i - k_1}{k_1 + k_2 i}} \qquad (4\cdot5)$$

We thus have:—

To the skew-symmetric self-dual null tensor whose components are given by (4·3) *with the additional condition* $k_1^2 + k_2^2 + k_3^2 = 0$, *corresponds the spinor* $(\bar{\psi}_1, \bar{\psi}_2)$ *where*

$$\frac{\bar{\psi}_1}{\bar{\psi}_2} = \sqrt{\frac{k_2 i - k_1}{k_1 + k_2 i}} \qquad (4\cdot6)$$

(4·5) and (4·6) correspond to the results of Van der Waerden and Whittaker respectively.

GENERALISATION OF A THEOREM OF PILLAI-SELBERG

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Introduction

Let $N^{2}_{r,t}(x)$ denote the number of square-free integers not exceeding x, whose number of prime factors belong to the residue class t modulus r. Pillai[1] and Selberg[2] have both proved that

$$N^{(2)}_{r,t}(x) \sim \frac{6}{\pi^2}\,\frac{x}{r}.$$

The purpose of the present paper is to show that by extending Pillai's reasoning, the above result can be generalised to kth power-free integers also ; a kth power-free integer is one which is not divisible by the kth power of any integer except unity. When $N^{k}_{r,t}(x)$ denotes the number of kth power-free integers not exceeding x, the number of whose prime factors (taking into consideration the degree of multiplicity also) belong to the residue class t modulus r, we have the

Theorem : $\quad N^{(k)}_{r,t}(x) \sim x/\zeta(k)$

where $\quad \zeta(k) = \sum_{n=1}^{\infty} \frac{1}{n^k}.$

Thus the theorem of Pillai-Selberg is a particular case of the theorem with $k = 2$.

Notation : In what follows by A is meant the appendix of Pillai's paper, attributed by him to have been due to Dr. Chowla.

Let $\quad \eta = e^{2\pi i s/r} \qquad (s = 1, \ldots r-1)$

$\lambda_r(n) = \eta^{t(n)}$ where $t(n)$ is the total number of prime factors of n, each prime factor being counted according to its degree of multiplicity.

$$L_r(n) = \sum_{n=1}^{x} \lambda_r(n)$$

$$L^{(k)}_r(n) = \sum_{n=1}^{x}{}' \lambda_r(n)$$

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[1] S. S. Pillai, " Generalisation of a Theorem of Mangoldt," *Proc. Ind. Acad. Sci.* (A), 1940, **11**, 13–20.

[2] S. Selberg, " Zur Theorie der quadratfreien Zahlen," *Math. Zt.*, 1939, **44**, 306–18.

where the summation Σ' is extended over all the $Q^k(x)$ kth power-free in tegers less than or equal to x.

$\mu(m)$ denotes the well-known Möbius's function.

Proof of the theorem : For the proof of the theorem we require the following lemmas.

Lemma 1 :

$$N_{r,1}^{(k)}(x) + N_{r,2}^{(k)}(x) + \ldots + N_{r,r}^{(k)}(x) = Q^{(k)}(x)$$

and $$Q^{(k)}(x) \sim \frac{1}{\zeta(k)} \cdot x$$

Proof : The first part of the lemma follows immediately from the definition. To prove the second part we note that

$$\sum_{\substack{m,u \\ m^k u = n}} \mu(m) = \begin{cases} 1 \\ \text{or} \\ 0 \end{cases}$$

according as n is or is not kth power-free.

Hence

$$\begin{aligned} Q^{(k)}(x) &= \sum_{n=1}^{x} \sum_{\substack{m,u \\ m^k u = n}} \mu(m) \\ &= \sum_{m=1}^{x^{k/1}} \mu(m) \sum_{u=1}^{[x/m^k]} 1 \\ &= \sum_{m=1}^{x^{1/k}} \mu(m) \left(\frac{x}{m^k} + \theta_m\right), \quad \text{where } 0 \leqslant \theta_m < 1, \\ &= x \sum_{m=1}^{x^{1/k}} \frac{\mu(m)}{m^k} + O(x^{1/k}) \\ &= x \frac{1}{\zeta(k)} + O\left(x \cdot \sum_{m > x^{1/k}} \frac{1}{m^k}\right) + O(x^{1/k}) \\ &= \frac{1}{\zeta(k)} x + O(x^{1/k}) \end{aligned}$$

Lemma 2 : $L_r(x) = 0(x)$

This result is given in **A**.

Lemma 3 : $L_r^{(k)}(x) = 0(x)$.

Proof : From the definition of $t(n)$ it is easily seen that if $n = m^k u$, then

$$t(n) = k \cdot t(m) + t(u)$$

Now,

$$\mathrm{L}_r^{(k)}(x) = \sum_{u=1}^{x} \eta^{t(u)} \sum_{\substack{m,u \\ m^k u = u}} \mu(m)$$

$$= \sum_{m=1}^{x^{1/k}} \mu(m)\, \eta^{kt(m)} \sum_{u=1}^{[x/m^k]} \eta^{t(u)}$$

$$= \sum_{m=1}^{x^{1/k}} \mu(m)\, \eta^{kt(m)}\, \mathrm{L}_r\left(\left[\frac{x}{m^k}\right]\right) \tag{1}$$

From lemma 2 since $\mathrm{L}_r(x) = 0(x)$, we have corresponding to every positive number ϵ, however small, an integer X_ϵ such that

$$|\mathrm{L}_r(x)| < \epsilon \text{ for all } x \geqslant \mathrm{X}_\epsilon.$$

Hence

$$\left|\mathrm{L}_r\left(\left[\frac{x}{m^k}\right]\right)\right| < \epsilon \cdot \frac{x}{m^k} \text{ if } \frac{x}{m^k} \geqslant \mathrm{X}_\epsilon. \tag{2}$$

and is less than $\frac{x}{m^k} < \mathrm{X}_\epsilon$ otherwise.

Hence the number of m's $\leqslant x^{1/k}$ for which (2) is not satisfied is atmost.

$$x^{1/k}\left(1 - \frac{1}{\mathrm{X}_\epsilon^{1/k}}\right) < \epsilon\, x/\mathrm{X}_\epsilon \quad \text{for all } x \geqslant \mathrm{Y}_\epsilon.$$

Hence the absolute value of sum (1) is less than

$$\left|\sum_{m > (x/\mathrm{X}_\epsilon)^{1/k}}^{x^{1/k}} \mu(m)\, \eta^{kt(m)}\, \mathrm{L}_r\left(\left[\frac{x}{m^k}\right]\right)\right| + \left|\sum_{m=1}^{(x/\mathrm{X}_\epsilon)^{1/k}} \mu(m)\, \eta^{kt(m)}\, \mathrm{L}_r\left(\left[\frac{x}{m^k}\right]\right)\right|$$

$$< x^{1/k}\left(1 - 1/\mathrm{X}_\epsilon^{1/k}\right)\mathrm{X}_\epsilon + \epsilon \cdot x \sum_{m=1}^{\infty} \frac{1}{m^k}$$

$$< \mathrm{C}\, \epsilon\, x \text{ for all } x \geqslant \mathrm{Max}\,(\mathrm{X}_\epsilon, \mathrm{Y}_\epsilon),$$

where C is a positive absolute constant. This proves the lemma.

Proof of the theorem : Arguing as in A we have the theorem from lemmas 1 and 3.

CHEMICAL INVESTIGATION OF INDIAN FRUITS

Part I. Bitter Principles of Pamparapanas (Indian Shaddock)

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The bitter taste of the fruits of the citrus group has been attributed to the existence of certain crystalline compounds the most important of which is naringin. Their study is of great interest in connection with the fruit industry. Though some element of bitterness is agreeable too much of it is a serious disadvantage. Two important points to be noted in this connection are (1) the bitter principles are found to reside mostly in the peels, rags (placenta and vascular bundles) and the seeds and (2) they are capable of conversion into non-bitter derivatives. The second phenomenon takes place particularly when the fruit ripens or when it is stored. There is therefore large scope for producing fruit juices without much bitterness by suitably adjusting the conditions. Further, the by-products, peels and seeds have found use in medicine mainly because of the existence of bitter principles in them.

Pamparapanas (Indian Shaddock) is a very large sized fruit commonly available in the coastal tracts. The peels are thick, with definite flavedo and albedo and the cellulose coatings enclosing the different sections can be easily removed by hand. The seeds are large and have a rough surface. The peels and rags are found to contain naringin as the bitter principle and in this respect this fruit resembles the grape fruit. In appearance, the nature of the different parts and other characteristics, however, the two fruits differ markedly. Regarding the peels of pamparapanas the method that is usually advocated for the preparation of naringin from the peels of the grape fruits is not quite suitable.[1] A preliminary extraction of the dry sample with ether considerably improves the efficiency of the subsequent extraction with aqueous alcohol. This is due to the removal of the oily and resinous matter. The above operation is not necessary in the case of the rags since they contain very little of oil in them. The fresh wet rags contain a high percentage of naringin (1%) and hence during manufacture of the juice great care has to be taken to avoid crushing these rags and extracting them.

The seeds from which the oil had been removed by extraction with light petroleum were employed for studying the bitter principles. Further extraction with alcohol removed all the bitterness of the seeds. The bitter components could be divided into two parts: (1) water-soluble and (2) water-insoluble. The first portion was identified as naringin and the second as a mixture of limonin and isolimonin. It may be remarked here that the presence of the last two in orange kernels was noted by Koller and Czerney[2] and that Feist and Overberg[3] recorded the presence of limonin in lemon pips. The occurrence of naringin in citrus seeds does not seem to have been observed till now. The point of interest is that naringin is intensely bitter and because of its solubility in water its taste is readily felt. On the other hand limonin and isolimonin are sparingly soluble in water and hence the solids when placed on the tongue do not give rise to the bitter taste. However when an alcoholic solution is diluted with a large volume of water, the dilute solution tastes markedly bitter. It is possible therefore that the marked bitterness of the seeds is mainly due to the naringin though the others may also add to it.

Naringin isolated from the different parts of the pamparapanas fruit was identified by a detailed study of its composition, properties and reactions and by comparison with an authentic sample of grape fruit naringin. The investigation definitely establishing the final constitution of naringin as a glycoside having the disaccharose group in the seventh position of naringenin has already been reported.[5] Though limonin has been known for a long time as the bitter principle of lemon seeds the first detailed investigation was published by Koller and Czerney[2] in 1936. They obtained it from orange kernels and gave the molecular formula as $C_{23}H_{26}O_7$, the melting point as 280° and the specific rotation as $-142°$. Immediately after, Feist and Overburg[3] gave a brief account of the properties of citrolimonin obtained from lemon seeds. This seems to be the same as limonin. The melting point however was given higher as 302°, the rotation as $-135°$ and the molecular formula as $C_{26}H_{30}O_8$. Koller and Czerney also isolated a small quantity of a second bitter principle called isolimonin to which they gave the molecular formula $C_{23}H_{28}O_7$. More recently Higby[4] has reported that isolimonin occurs as the main bitter principle of the peels, rags and seeds of Navel oranges and limonin in Valencia oranges, that the two are isomeric and that the former yields on hydrolysis with alkali limonin as one of the products.

The seeds of the shaddock probably owe their main part of the bitterness to the presence of naringin. However a mixture of limonin and isolimonin occurs to the extent of about 0·6% of the dry weight of the seeds and of

this isolimonin is only in very small quantities, about 0·03%. The separation of the two water-insoluble bitter compounds was effected by utilising the marked differences in solubility in alcohol and benzene. Our results relating to the composition and properties of limonin agree with those of Higby. The correct melting point of limonin seems to be 292° and the molecular formula $C_{26}H_{30}O_8$. The specific rotation recorded by Koller *et al.* and Feist *et al.*, is too high and differs considerably from the values obtained by Higby. We were first under the impression that this was due to the different solvents that they employed. On examining this point using acetone, chloroform and acetylene tetrachloride the correct rotation was found to be only about 110°, the high error of the early investigators being obviously due to the small quantities of substances that they employed and the volatility of the solvent.

The resemblance between limonin and isolimonin is rather close. They give the same reactions with acids and alkalies and have more or less the same rotation. Both seem to possess 2 lactone groups. Hence they should possess very closely related molecular constitutions. This is further supported by the fact that Higby has been able to prepare limonin from isolimonin. Besides melting point and solubility, other differences do not seem to be very definite. A number of attempts were made to decide if coumarin rings existed in the molecule of limonin. Experiments carried out under various conditions using methyl alcohol, potash and dimethyl sulphate did not yield any product of methylation. Hence the presence of α-pyrone rings is doubtful though not impossible.

Experimental

The fruits were obtained from Rajahmundry during the months of September and October. As soon as they arrived in the laboratory they were peeled out, the sections opened and the rags and seeds separated from the juicy portions as much as possible. The peels and the rags were preserved separately in wide-mouthed bottles with a little formalin. The seeds were dried and stored.

Analysis of the Peels.—The entire peels including the albedo and flavedo were employed. The fresh samples were cut into bits, crushed in a mortar and analysed adopting the methods of the Association of Official Agricultural Chemists for feeding stuffs. The results are presented in the form of a table along with those obtained for grape fruit peel by Poore.[1]

	Fresh peels of Pamparapanas per cent.	Grape fruit peels (fresh) per cent.
Total solids	24·12	16·71
Mineral matter	2·08	0·74
Acids as citric acid	1·67	0·74
Crude fat (ether extract)	0·27	0·28
Proteins (N × 6·24)	1·51	1·13
Sugars as invert sugar	4·54	6·35
Starch as invert sugar	6·55	..
Pentosans	2·82	0·83
Crude fibre	3·86	1·71
Naringin	0·13	0·4
P_2O_5	0·20	..
K_2O	0·43	..

The peels of the shaddock contain more solid matter and a higher proportion of carbohydrates, proteins and mineral salts and hence they are better as cattle fodder when large quantities are available as by-products in industry than grape fruit peels. Further they contain less of the bitter principle, naringin and hence are less objectionable.

Isolation of Naringin from the Peels.—The method of Poore[1] employing the fresh peels of the grape fruits and using methylated spirits for extraction was not found to be suitable in the present case. There was considerable difficulty in the separation of naringin from the extract due to the presence of oily and resinous matter. This was overcome by employing the dried peels and subjecting them to a preliminary extraction with ether.

Sun dried peels (800 g.) were ground to powder in a laboratory mill and kept soaked in ether for 12 hours. The ether extract was decanted and more ether added to the residue. The process was repeated twice again in order to remove as completely as possible ether-soluble matter. The ether extract was distilled to recover the solvent and the residue was examined. It did

not taste bitter and hence was discarded. The residual peels were then boiled under reflux with methylated spirits (about 1 litre) for two hours and the extract filtered. The solid residue was twice again extracted with alcohol in a similar manner and the combined extracts were treated with a slight excess of a saturated solution of neutral lead acetate. The precipitate that was formed was filtered, the filtrate heated nearly to boiling and a current of hydrogen sulphide passed in order to precipitate the excess of lead. After removing lead sulphide the clear solution was concentrated under reduced pressure to syrupy liquid. It was quickly filtered while hot and allowed to crystallise in an ice chest. After standing for about a week the crystals were collected and recrystallised from a small quantity of water. The substance was exceedingly bitter, appeared as colourless rectangular plates and melted at 83°. The yield of the pure substance was 0·13% of the fresh peels and 0·54% of the dry sample.

Naringin from the Rags.—The rags were far more bitter than the peels and the extraction of the bitter principle was easier for the reason that there was very little of oily matter. Preliminary drying and extraction with ether were therefore unnecessary. The fresh and wet rags were crushed in a mortar, extracted with boiling alcohol and the bitter principle isolated as in the case of the peels. The yield of the crystalline material was rather high (1%) and the substance was identical with the one obtained above.

The crystalline bitter substance was soluble to some extent in cold water, readily in boiling water, acetone and alcohol and insoluble in ether, light petroleum and benzene. It gave a yellow colour with aqueous sodium hydroxide, red colour with ferric chloride or with a reducing mixture of magnesium and hydrochloric acid. In the air-dry condition it melted at 83° but after drying at 110° the melting point was 172°. In alcoholic solution $[\alpha]_D$ was 89·5°. On hydrolysis with dilute sulphuric acid it gave a non-bitter aglucone melting at 244°. The sugars that were produced as the other products of hydrolysis were recognised as glucose and rhamnose from their osazones. From all these properties the substance was identified as naringin and this was confirmed by comparison with an authentic sample of grape fruit naringin.

The Bitter Principles of the Seeds.—The seeds that were dried in the sun were ground in a laboratory mill to a coarse powder and analysed. The following results indicate the general composition: Oil 39%, sugars 0·4%, proteins 8·8% and ash 2·9%.

The seed powder (900 g.) was extracted in a soxhlet with light petroleum in order to remove all the oil. The fat-free residue was quite bitter to

the taste. It was subsequently boiled with methylated spirits for about 12 hours, filtered and the extraction repeated a second time with fresh spirits. The combined extracts were distilled on a water-bath almost to dryness under reduced pressure. The solid residue appeared to be a mixture of crystalline and amorphous substances and tasted strongly bitter. When it was extracted repeatedly with hot water a colourless crystalline residue was left behind and the comparatively non-crystalline portion (A) went into solution in water.

The water-insoluble crystalline solid seemed to be a mixture with an indefinite melting point. By repeated extraction with cold alcohol it was separated again into two fractions (B and C). The residue left unextracted (B) was sparingly soluble in alcohol and more easily soluble in acetic acid and acetone. It was purified by boiling with small quantites of alcohol and finally crystallised from glacial acetic acid. Large colourless rectangular prisms and tablets melting at 292–94° (decomp.) were thus obtained. It contained no N, S, halogens or methoxyl groups. (Found: C, 66·6; H, 6·2; molecular weight by Rast's method 458: $C_{26}H_{30}O_8$ requires C, 66·4; H, 6·4 and molecular weight 470.) $[\alpha]_D$ in acetone solution was $-110°$, in chloroform $-113°$ and in acetylene tetrachloride $-112°$. The value given by Higby for the alcoholic solution is -106–114 whereas Koller and Czerney reported a value of $-142°$ for the solution in methylene chloride. The higher value seems to be in error. The substance was insoluble in cold aqueous potash and dissolved on boiling. From this solution it could be recovered by acidification. It could not be acetylated with sodium acetate and acetic anhydride. It was therefore identified as limonin.

Limonin is unaffected by concentrated hydrochloric acid, but dissolves in strong nitric acid with a pale yellow colour and with concentrated sulphuric acid it produces a remarkably deep red solution, the colour of which disappears on dilution with water. The crystals do not taste, but a solution in very dilute alcohol is very bitter. It does not respond to the test for the flavanone group with magnesium and hydrochloric acid and does not reduce Fehlings solution. Attempts to methylate it with dimethyl sulphate and potash in the presence of methyl alcohol or acetone were unsuccessful.

The fraction (C) which is easily soluble in cold alcohol was recovered by distilling off the solvent. By repeated recrystallisation first from benzene and then from aqueous alcohol, it was obtained as colourless crystals (rhombic and rectangular plates) melting at 258–60° (decomp.) and the mixed melting point with limonin was depressed. (Found: C, 65·9; H, 6·4; $C_{26}H_{30}O_8$ requires C, 66·4; H, 6·4%.) $[\alpha]_D$ in acetone was $-108°$ (Higby

— 112°). It tasted bitter in very dilute alcoholic solution and in all respects agreed with the description of isolimonin. It gave the same reaction with alkali and acids as limonin.

The total yield of the limonin-isolimonin mixture was about 0·6% on the weight of the air-dry seeds of which a very small part was isolimonin.

The water-soluble bitter fraction (A) was isolated by concentrating the solution under reduced pressure to a small bulk and finally removing the last portion of water by evaporation in a vacuum desiccator. The solid residue which was strongly bitter, was obtained pure by repeated crystallisation from water and was identified as naringin. There was considerable loss during the crystallisation and with a view to estimate the quantity present, the amorphous product obtained in another experiment was hydrolysed with dilute sulphuric acid and the sparingly soluble aglucone thereby obtained was dried and weighed. From this naringin was found to be present to the extent of 0·15% on the weight of the air-dry seeds.

Summary

Convenient methods have been worked out for the isolation of the bitter principles of the peels, rags and the seeds of pamparapanas (Indian Shaddock). The first two contain naringin to the extent of 0·13 and 1% respectively whereas in the seeds naringin (0·15%) and limonin (about 0·6%) are found to be the most important bitter components besides small amounts of isolimonin. Some properties of limonin and isolimonin have been studied.

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STUDIES IN CHLORALAMIDES

Part II. Chloral Nitro- and Chloral Bromo-Salicylamides

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A detailed study of chloral salicylamide and its methyl ether has been made by previous authors.[1] The present paper deals with a study of nitro substitution products and the bromo substitution products of these compounds. The constitutions of the various nitro chloral salicylamides obtained by the nitration of chloral salicylamide and its methyl ether and of the various bromo chloral salicylamides obtained by the bromination of chloral salicylamide and its methyl ether were established by hydrolysing them to the known salicylic acids and their constitutions were further confirmed by directly condensing the various known nitro- and bromo-salicylamides and their methyl ethers with chloral.

It has been found by the present authors that during nitration and bromination of chloral salicylamide the para directing influence of the OH group which is clearly obvious in nitration of salicylic acid[2] is considerably lessened by the presence of $CONH \cdot CH \cdot (OH) \cdot CCl_3$ group in the ortho position. Thus chloral salicylamide when nitrated gives mainly chloral 3-nitro-salicylamide together with only a small quantitiy of 5-nitro-salicylamide instead of its chloral condensation product and chloral salicylamide when brominated gives very little 5-bromochloral salicylamide the main product being a compound which gives 3-bromo salicylic acid on hydrolysis.

Further if chloral-3-nitro salicylamide is brominated in order to get chloral-3-nitro-5-bromo-salicylamide, bromine enters position 5 with a simultaneous detachment of the chloral group and 3-nitro-5-bromo-salicylamide is obtained. 5-nitro salicylamide and 5-bromo-salicylamide cannot be condensed with chloral in order to get chloral-5-nitro-salicylamide and chloral-5-bromo-salicylamide respectively; while the 3-nitro salicylamide and 3-bromc-

[1] H. P. Kaufmann, *Ach. Pharn*, 1927, **265**, 226–38.; A. N. Meldrum and Deodhar, *J. Ind. Chem. Soc.*, 1934, **11**, 529.

[2] Hirwe and Meldrum, *J. Ind. Chem. Soc.*, 1930, **1**, 887.

salicylamide condense easily. However, it may be noted with interest that if the nuclear OH group is changed into a $-OCH_3$ group, then the product of nitration and of bromination of chloral O-methoxy benzamide are exclusively 5-nitro chloral 2-methoxy benzamide and 5-bromo chloral-2-methoxy benzamide respectively. This is undoubtedly due to the stronger para directing influence of the methoxyl group.

Experimental

Chloral-3-nitro salicylamide—

1. A mixture of chloral salicylamide (20 g.) and dilute nitric acid (40 c.c., sp. gr. 1.2) was kept at room temperature for four days when a yellow solid, a mixture of chloral-3-nitro-salicylamide and 5-nitro-salicylamide was obtained. On fractionation from alcohol yellow cubes separated (yield 10 g.) m.p. 154°. It gave red colour with ferric chloride. (Found : Cl 32·1, N 8·5; $C_9H_9O_5N_2Cl_3$ requires Cl 32·3, N 8·5 per cent.)

The mother liquor from the above experiment on further concentration gave yellow needles, m.p. 224–25° identified as 5-nitro salicylamide.

Hydrolysis.—The foregoing chloral compound (0.5 g.) was refluxed with sodium hydroxide solution (10 per cent. 10 c.c.) for two hours. On acidification a solid was obtained which crystallised from water in needles, m.p. 128°, identified as 3-nitro salicylic acid.

2. A mixture of 3-nitro salicylamide (5 g.) and choloral (5 g.) was heated on a flame till a clear solution was obtained. It was kept overnight at room temperature when it set to a transparent sticky mass, which gave a solid (7 g.) on being washed with water. It was recrystallised from alcohol in yellow cubes m.p. 154° identical with above.

Sodium Salt.—($NO_2 \cdot C_6H_3 \cdot ONa \cdot CO \cdot NH \cdot CH \cdot ONa \cdot CCl_3$).

A red solid, very soluble in water. (Found; Na 11·1, H_2O 8·5; $C_9H_5O_5N_2Na_2Cl_3$, $2H_2O$ requires Na 11·2 and H_2O 8·8 per cent.)

Potassium Salt.—($NO_2C_6H_3OK \cdot CO \cdot NH \cdot CH \cdot OK \cdot CCl_3$.)

A red solid very soluble in water. (Found: K 19·1 ; $C_9H_5O_5N_2Cl_3K_2$ requires K 19·2 per cent.)

Calcium Salt.—To a solution of chloral 3-nitro salicylamide in dilute ammonium hydroxide was added a solution of calcium chloride when a yellow solid separated which crystallised from water in yellow granules with five molecules of water. This water of crystallisation could not be removed at lower temperatures and even under reduced pressure. At higher

temperatures the salt decomposes. (Found: Ca 8·7; $C_9H_5O_5N_2Cl_3Ca$, $5H_2O$ requires Ca 8.7 per cent.)

Chloral 3-nitro 5-bromo salicylamide—

1. A mixture of 3-nitro 5-bromo salicylamide (10 g.) and chloral (10 g.) was heated under reflux at 140–50° until a clear solution was obtained and further kept overnight at room temperature. The solid obtained (15 g.) was recrystallised from alcohol in brownish yellow cubes, m.p. 155°(decomp.). (Found: silver halide 151·0, N 6·8; $C_9H_6O_5N_2Cl_3Br$ requires silver halide 151·5 and N 6·8 per cent.)

2. The compound could not be prepared by the bromination of chloral 3-nitro salicylamide in glacial acetic acid. The compound obtained was 3-nitro 5-bromo salicylamide instead of its chloral condensation product.

Chloral 3·5 dinitro salicylamide—

1. Chloral salicylamide (15 g.) in concentrated sulphuric acid (15 g.) was nitrated at about 10° with fuming nitric acid (5 g., d. 1·45) added in small quantities each time. The mixture was then kept in the refrigerator for twelve hours and then poured over crushed ice when a yellow solid separated. It was crystallised from alcohol in yellow granules, m.p. 154° (decomp.). It gave red colour with ferric chloride. (Found: Cl 28·3, N 11·3; $C_9H_6O_7N_3Cl_3$ requires Cl 28·4, N 11·2 per cent.)

The compound on hydrolysis with hot sodium hydroxide solution in the usual manner gave 3: 5-dinitro salicylamide.

2. 3: 5 dinitro salicylamide (10 g.) was condensed with chloral (10 g.) in the usual manner. The solid obtained (14 g). crystallised from alcohol in yellow granules, m.p. 154° identical with the above.

Chloral 5-nitro 2-methoxy benzamide—

1. Sulphuric acid (6 g., d. 1·84) was added with constant stirring to a solution of chloral methoxy benzamide (2 g.) in nitric acid (d. 1·45, 5 g.) at about 25°. The solution was then poured on to crushed ice when a solid (2 g.) separated which crystallised from alcohol in white needles, m.p. 155° (decomp.). (Found: Cl 31·0, N 8·4; $C_{10}H_9O_5N_2Cl_3$ requires Cl 31·0, N 8·5 per cent.)

This compound on hydrolysis gave 5-nitro-2-methoxy benzamide.

2. 5-nitro-2-methoxy benzamide (10 g.) was condensed with chloral (10 g.) in the usual manner. The solid obtained crystallised from alcohol in white shining needles, m.p. 155° (decomp.) identical with the above.

Chloral 3-nitro 2-methoxy benzamide—

A mixture of 3-nitro 2-methoxy benzamide (8 g.) and chloral (8.g) were condensed together in the usual manner. The solid which separated, crystallised from alcohol in big transparent yellowish parallelograms, m.p. 106° (decomp.). (Found: Cl 31·1, N 8·3; $C_{10}H_9O_5N_2Cl_3$ requires Cl 31·0, N 8·5 per cent.)

Chloral 3: 5-dinitro 2-methoxy benzamide—

1. Fuming nitric acid (5 g., d. 1·45) was added with constant stirring to a solution of chloral 2-methoxy benzamide (5 g.) in concentrated sulphuric acid (15 c.c., d. 1·84) at 10°. After keeping for twelve hours in the refrigerator, it was poured on to crushed ice when a yellow solid (6 g.) separated. It crystallised from alcohol in yellow rectangular plates, m.p. 142–43° (decomp.). (Found: Cl 27·5, N 10·7; $C_{10}H_8O_7N_3Cl_3$ requires Cl 27·4, N 10·8 per cent.)

This compound on hydrolysis gave 3: 5 dinitro salicylamide.

2. 3: 5 dinitro 2-methoxy benzamide (6 g.) was condensed with chloral in the usual manner. The solid crystallised from alcohol in yellow needles, m.p. 143° identical with the above.

Chloral 5-bromo salicylamide—

Bromine vapour (8·7 g.) was very slowly aspirated through a solution of chloral salicylamide (15 g.) in glacial acetic acid at room temperature and the solution kept overnight. A solid separated which melted at 239°. (The constitution of this compound has not yet been investigated.) The acetic acid mother liquor on dilution gave a solid which was a mixture and which on fractionation from alcohol gave small cubes, m.p. 150–52°. (Found: silver halide, 171·2; $C_9H_7O_3NCl_3Br$ requires silver halide 170·2 per cent.)

This compound on hydrolysis gave 5-bromo salicylic acid.

Chloral 3: 5 dibromo salicylamide—

1. Bromine vapour (40 g.) was slowly aspirated through a solution of chloral salicylamide (35 g.) in glacial acetic acid with traces of iodine as a catalyst. The solution on dilution with water gave a solid which crystallised from alcohol in plates, m.p. 158–60°. (Found: silver halide 180·8, N 2·9; $C_9H_6O_3NCl_3Br_2$ requires silver halide 182·3, N 3·2 per cent.)

This compound on hydrolysis gave 3: 5 dibromo-salicylic acid.

2. 3: 5 dibromo salicylamide (10 g.) was condensed with chloral (10 g.) in the usual manner. The solid crystallised from alcohol in plates, m.p. 160° identical with the above.

Chloral 3-bromo salicylamide—

3-bromo salicylamide (10 g.) and chloral (10 g.) were condensed together in the usual manner. The solid crystallised from alcohol in cubes, m.p. 161°. (Found: silver halide, 170·1; $C_9H_7O_3NCl_3Br$ requires silver halide 170·2 per cent.)

5-bromo 2-methoxy chloral benzamide—

1. Bromine vapour (5 g.) was slowly aspirated through a solution of chloral 2-methoxy benzamide (10 g.) in glacial acetic acid. The mixture was allowed to stand overnight; on dilution a solid was obtained which crystallised from alcohol in needles, m.p. 147–48°. (Found: silver halide 163·7, N 3·4; $C_{10}H_9O_3N\ Cl_3Br$ requires silver halide 163·9, N. 3·7 per cent.)

The compound on hydrolysis gave 5-bromo 2-methoxy benzoic acid.

2. 5-bromo 2-methoxy benzamide (10 g.) was condensed with chloral in the usual way. The solid obtained, crystallised from alcohol in needles, m.p. 147–48° identical with the above.

Chloral 3-bromo 2-methoxy benzamide—

3-bromo 2-methoxy benzamide (10 g.) was condensed with chloral (10 g.) in the usual manner. The solid crystallised from alcohol in flakes, m.p. 129°. (Found: silver halide 162·5, $C_{10}H_9O_3NCl_3Br$ requires silver halide 163·9 per cent.)

Chloral 3: 5-dibromo 2-methoxy benzamide—

3: 5 dibromo 2-methoxy benzamide (10 g.) was condensed with chloral (10 g.). The solid crystallised from alcohol in hexagonal yellow plates, m.p. 156°. (Found: silver halide, 179·4; $C_{10}H_8O_3NCl_3Br_2$ requires silver halide 176·5 per cent.)

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